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WO 2004/034809 A1

(54) Title: FISH ENSILAGE AND PRODUCT FOR PREVENTING GAS FORMATION IN FISH ENSILAGE

(57) Abstract: The present invention relates to fish ensilage comprising 0.05 - 3 weight % of a formulation that prevents gas formation comprising sulphite and/or disulphite and/or bisulphite and optionally nitrite and/or benzoate. The fish ensilage will comprise 0.05 - 0.20 weight % sulphite and/or disulphite and/or bisulphite, 0 - 0.05 weight % nitrite and 0 - 0.50 weight % benzoate. A foam inhibitor may be present in the ensilage in an amount of 0.0005 - 0.02 weight %. The invention also comprises a product for preventing gas formation in fish ensilage, where said product preferably comprises 2 - 50 weight % sulphite and/or disulphite and/or bisulphite, 0 - 10 weight % nitrite, 0 - 25 weight % benzoate, 0 - 1 weight % foam inhibitor, the balance being water.

Fish ensilage and product for preventing gas formation in fish ensilage

The present invention relates to a fish ensilage having improved storage properties and a product for preventing gas formation in fish ensilage.

During production and transportation of fish ensilage extreme gas formation in the ensilage occasionally occurs. Due to the properties of the ensilage (oil and water) this results in large bubbles (boiling) and foaming, which creates serious handling problems.

WO 01/06869 relates to a process and a material for inhibition of gas formation in fish ensilage where an effective amount of an agent, which inhibits microbial growth, is added to the fish ensilage. A preferred embodiment of the process relates to addition of sodium benzoate and a preferred material according to the invention is a fish ensilage fluid comprising sodium benzoate.

The effect of sodium benzoate is not sufficient to inhibit the boiling enough to keep it on an acceptable level, and it would therefore be of interest to develop a formulation being able to sufficiently inhibit the gas formation and the consequences thereof. It would also be of interest to develop an effective foam inhibitor, either combined with the gas inhibition composition or as a separate agent.

The main object of the invention was to provide a fish ensilage, which would not have problems with gas formation and foaming during storage for a prolonged period of time.

Another object was to obtain a product, which would effectively prevent gas formation in fish ensilage.

It was a further object that the product should also prevent foaming in fish ensilage.

These and other objects of the invention were obtained by the fish ensilage and product as described below. The invention is further characterized by the patent claims.

Several factors may cause gas formation (boiling) in fish ensilage, for instance microbial activity with a resulting gas formation, CO_2 development from fish bones being dissolved in acid or enzymatic reactions.

Provided that the boiling primarily is caused by micro organisms, it should be possible to provoke boiling in fresh ensilage by inoculation of 1 – 50 weight % of a boiling ensilage or an ensilage, which has recently been boiling. This because the micro organisms from the boiling ensilage then would get new nutrients and multiply quickly under the right conditions and cause boiling in the fresh ensilage. In this way the inventors were able to investigate the effect of some selected formulations, assumed to inhibit boiling in fish ensilage. During the tests it was found that formulations comprising different forms of sulphite and possibly also nitrite and benzoate effectively inhibited boiling in the ensilage. Forms of sulphite that may be used are sulphite, disulphite (metabisulphite) and bisulphite. Cations could be sodium, potassium, magnesium, calcium or ammonium. The most preferred cations would be sodium and potassium. A fish ensilage comprising 0.05 – 3 weight % of the formulations that inhibited boiling, were found to be effective. When a foam inhibitor was added, either alone or in combination with the formulations that inhibited boiling, also the foaming of the fish ensilage was significantly reduced. Foam inhibitors comprise surface-active agents, which reduce the surface tension so that the foam bubbles burst.

The present invention will in its widest scope comprise a fish ensilage comprising 0.05 – 3 weight % of a formulation that prevents gas formation comprising sulphite and/or disulphite and optionally nitrite and/or benzoate. The fish ensilage will comprise 0.05 – 0.20 weight % sulphite and/or disulphite and/or bisulphite, 0 – 0.05 weight % nitrite and 0 – 0.50 weight % benzoate. The fish ensilage may also comprise a foam inhibitor in an amount of 0.0005 – 0.02 weight %.

The invention also comprises a product for preventing gas formation in fish ensilage, where said product comprises 2 – 50 weight % sulphite and/or disulphite and/or bisulphite, 0 – 10 weight % nitrite, 0 – 25 weight % benzoate, 0 – 1 weight % foam inhibitor, the balance being water.

The invention is further explained in the following figures and examples.

Fig. 1 shows gas formation in an experiment where different formulations were tested.

Fig. 2 shows gas formation for different concentrations of formulations.

Fig. 3 shows gas formation with optimised concentrations of the different formulations.

Fig. 4 shows gas formation in a specific formulation at different pH values.

Test system

It was necessary to have a reliable test system for establishing of boiling at different pH values and temperatures. Fish ensilage from a cold storage and fish ensilage that had earlier been boiling were mixed in glass bottles. The glass bottles with fish ensilage were sealed with a cork with a valve, and a tube was connected to the valve and placed in a measuring flask, which was filled with water and placed upside down in a beaker. The gas formation in the glass bottles was measured by reading the height of the water column. The test system was used in Examples 1 – 5. All tests were performed at room temperature.

Example 1

Example 1 relates to testing of different formulations suitable to inhibit gas formation. The test system as described above was used. Portions of 250 g "boiling" ensilage were used in each glass bottle. The pH of the ensilage was 3.8 – 3.9.

The following different formulations were tested:

B5 - Bensilox essence, which comprises 76 – 77 weight % propionic acid, 23 weight % benzoic acid, 0 – 1 weight % water, was added to the ensilage in a dosage of 0.5 weight %).

B6 – "Nutriox", which comprises 45 weight % calcium nitrate, 55 weight % water, was added to the ensilage in a dosage of 1.0 weight %.

B7 - Sodium benzoate, which comprises 26 weight % sodium benzoate, 74 weight % water, was added to the ensilage in a dosage of 1.0 weight %.

B8 – Nitrite, which comprises 25 weight % sodium nitrite, 75 weight % water, was added to the ensilage in a dosage of 0.5 weight %.

B9 – Sulphite, which comprises 10 weight % sodium sulphite, 90 weight water, was added to the ensilage in a dosage of 2 weight %.

B10 - Control without addition.

The gas volumes produced were registered at start, after 15 min, 30 min, 45 min, 60 min, 100 min, 160 min, 265 min and 390 min. Fig. 1 shows the gas formation in the different fish ensilages. At the end of the test, the pH in all of the glass bottles was measured and was in the range 3.8 – 4.0. From Fig. 1 it is seen that the gas formation increased rapidly when the formulations comprising Bensilox essence (B5), "Nutriox" (B6) and Sodium benzoate (B7) were added. The gas formation was significantly inhibited when formulations according to the invention comprising Sulphite (B9) or Nitrite (B8) were added to the ensilage.

Example 1 shows that there is significant prevention of gas formation in the ensilage with those formulations that comprise sulphite or nitrite.

Example 2

Example 2 relates to testing of different formulations. The same test system as previously described was used.

Two ensilages, one boiling and one fresh, were mixed in a ratio 1:1. pH was 3.2 and 4.8, respectively. 400 g of ensilage was added to each glass bottle.

The following concentrations of formulations were added to each bottle:

C1 – Bensilox essence, dosage 1 weight %.

C2 – Sodium benzoate, dosage 2 weight %.

C3 – "Nutriox", dosage 2 weight %.

C4 – Sulphite, dosage 2 weight %.

C11 – Control without addition.

C12 – Nitrite, dosage 0.25 weight %.

The gas volumes were registered at start, after 15 min, 30 min, 90 min, 135 min, 195 min and 840 min. Fig. 2 shows the gas formation in the ensilage comprising the different formulations. At the end of the test the pH in all of the glass bottles was measured and was in the range 3.5 – 3.7. From Fig. 2 it is seen that addition of Sulphite (C4) gave lowest gas formation, and also addition of Nitrite (C12) effectively inhibited the gas formation. The other tested formulations did not sufficiently prevent the gas formation in the ensilage.

Example 2 shows that the addition of formulations comprising sulphite or nitrite has an inhibitory effect on the boiling in the concentrations that were tested.

Example 3

Example 3 relates to tests with optimised concentrations of selected formulations. The same test system as previously described was used.

Fresh ensilage (not boiled and kept in a refrigerator overnight) and boiling ensilage (directly from a boat) were mixed in a relation 2:1. pH was 4.1. Portions of 400 g were transferred to glass bottles and the following formulations were added:

D1 – Bensilox essence, dosage 1 weight %.

D2 – Bensilox essence, dosage 1 weight %.

D3 – Nitrite, dosage 0.3 weight %.

D4 – Nitrite, dosage 0.3 weight %.

D5 – Sulphite, dosage 2 weight %.

D6 – Sulphite, dosage 2 weight %.

D7 – A formulation comprising 15 weight % sodium benzoate, 1.5 weight % sodium nitrite, 6 weight % sodium sulphite, 78.5 weight % water, dosage 1.6 weight %.

D8 – Formulation and dosage as in D7.

D9 - Control without addition.

D11 – Control without addition.

The gas volumes produced were registered at start, after 15 min, 35 min, 60 min, 90 min, 120 min, 150 min, 180 min, 340 min, 550 min, 710 min and 1270 min. pH was read in the bottles at the end of the test, the pH values for the different formulations were 2.1 – 4.8.

Fig. 3 shows the gas formation in the ensilage. As can be seen from the Figure, when Sulphite (D5, D6) or Nitrite (D3, D4) or a mixture comprising sulphite, nitrite and benzoate (D7, D8) were added to the ensilage, the gas formation was kept at a low level for a prolonged storage period.

Example 3 shows that formulations comprising sulphite or nitrite or a mixture comprising sulphite, nitrite and benzoate inhibit the boiling in the fish ensilage.

Example 4

Example 4 relates to a test of a foam inhibitor.

Boiling ensilage in portions of 150 g was transferred to 4 test tubes. To each test tube, different concentrations of a mixture of a foam inhibitor and Bensilox essence were added. The tested foam inhibitor was the commercial product Antraphon NE4582.

Of practical reasons, the test was performed using Bensilox essence as the gas inhibiting formulation, but the results regarding foaming are assumed to be similar for the other formulations according to the invention.

K1 – 0.1 weight % Bensilox essence with foam inhibitor (10 ppm final concentration).
K2 – 0.3 weight % Bensilox essence with foam inhibitor (30 ppm final concentration).
K3 – 1.0 weight % Bensilox essence with foam inhibitor (100 ppm final concentration).
K4 – Control without addition.

A continuous visual inspection was carried out, and a significant reduction of the foam was observed in the test tube with 100 ppm foam inhibitor (K3). The reduction was less in K1 and K2, and K4 had most foaming.

Example 5

Example 5 relates to tests of a specific formulation (H) comprising 8 weight % sodium sulphite, 10 weight % sodium benzoate, 2 weight % sodium nitrite and 80 weight % water in a number of samples from ensilage parties that were reported to "boil".

The same test system as previously described was used. Ensilage samples of approximately 500 g were divided in two equal sub samples. To one of the sub samples 1.25 weight % of the above formulation was added, while no additions were made to the second sub sample (control). The gas formation from the two sub samples was monitored during incubation in room temperature for 24 hours.

Fig. 4 shows the gas formation from untreated samples (controls) compared to that from their counterpart treated with the formulation during incubation in test system for 24 hours. The pH at onset of test is given in Table 1. The pH varied in the range 3.1 – 5.1.

Table 1

Ensilage sample	H2	H3	H6	H8	H9	H10	H14	H16
pH	4.7	3.9	3.4	5.1	3.1	3.2	3.9	4.6

Example 5 shows that addition of formulations comprising sulphite, nitrite and benzoate reduces or eliminates gas formation in ensilage over a wide range of pH values.

As can be seen from the above, the inventors have succeeded in arriving at an improved ensilage, which is possible to store for a prolonged period of time without having problems with gas formation and boiling. As shown by the above examples the ensilage and product according to the invention is substantially better that known ensilages and products with regard to gas formation and boiling. Also the foaming in the ensilage is reduced.

Claims

1. Fish ensilage,
characterized in that
said ensilage comprises 0.05 – 3 weight % of a formulation that prevents gas formation comprising sulphite and/or disulphite and/or bisulphite and optionally nitrite and/or benzoate.

2. Fish ensilage according to claim 1,
characterized in that
said ensilage comprises 0.05 – 0.20 weight % sulphite and/or disulphite and/or bisulphite, 0 – 0.05 weight % nitrite, 0 – 0.50 weight % benzoate.

3. Fish ensilage according to claim 1,
characterized in that
said ensilage also comprises a foam inhibitor.

4. Fish ensilage according to claim 3,
characterized in that
the content of foam inhibitor is 0.0005 – 0.02 weight %.

5. Product for preventing gas formation in fish ensilage,
characterized in that
said product comprises 2 – 50 weight % sulphite and/or disulphite and/or bisulphite, 0 – 10 weight % nitrite, 0 – 25 weight % benzoate, 0 – 1 weight % foam inhibitor, the balance being water.

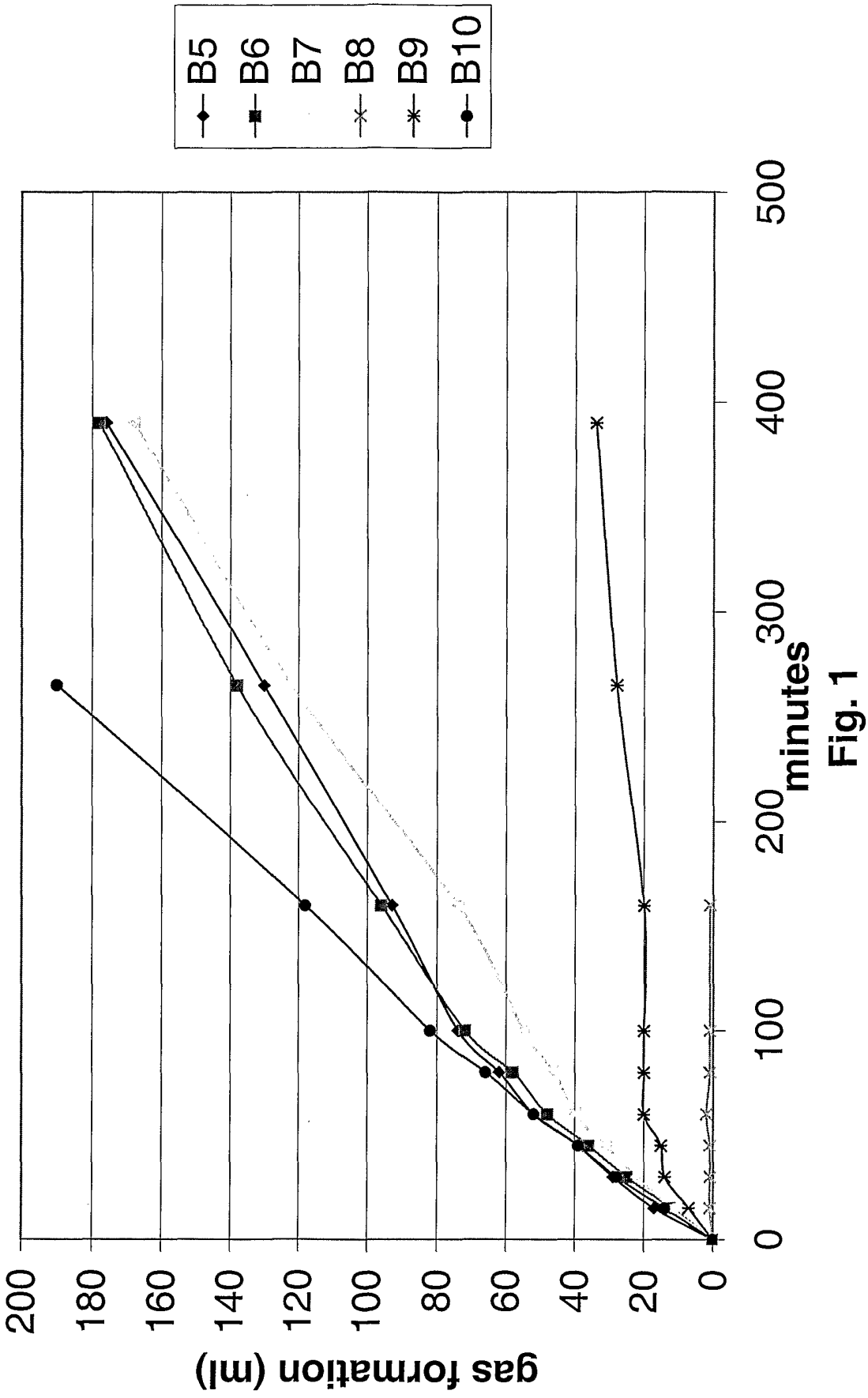
B5
B6
B7
B8
B9
B10
gas formation (ml)
0
20
40
60
80
100
120
140
160
180
200
0
100
200
300
400
500
minutes

Fig. 1

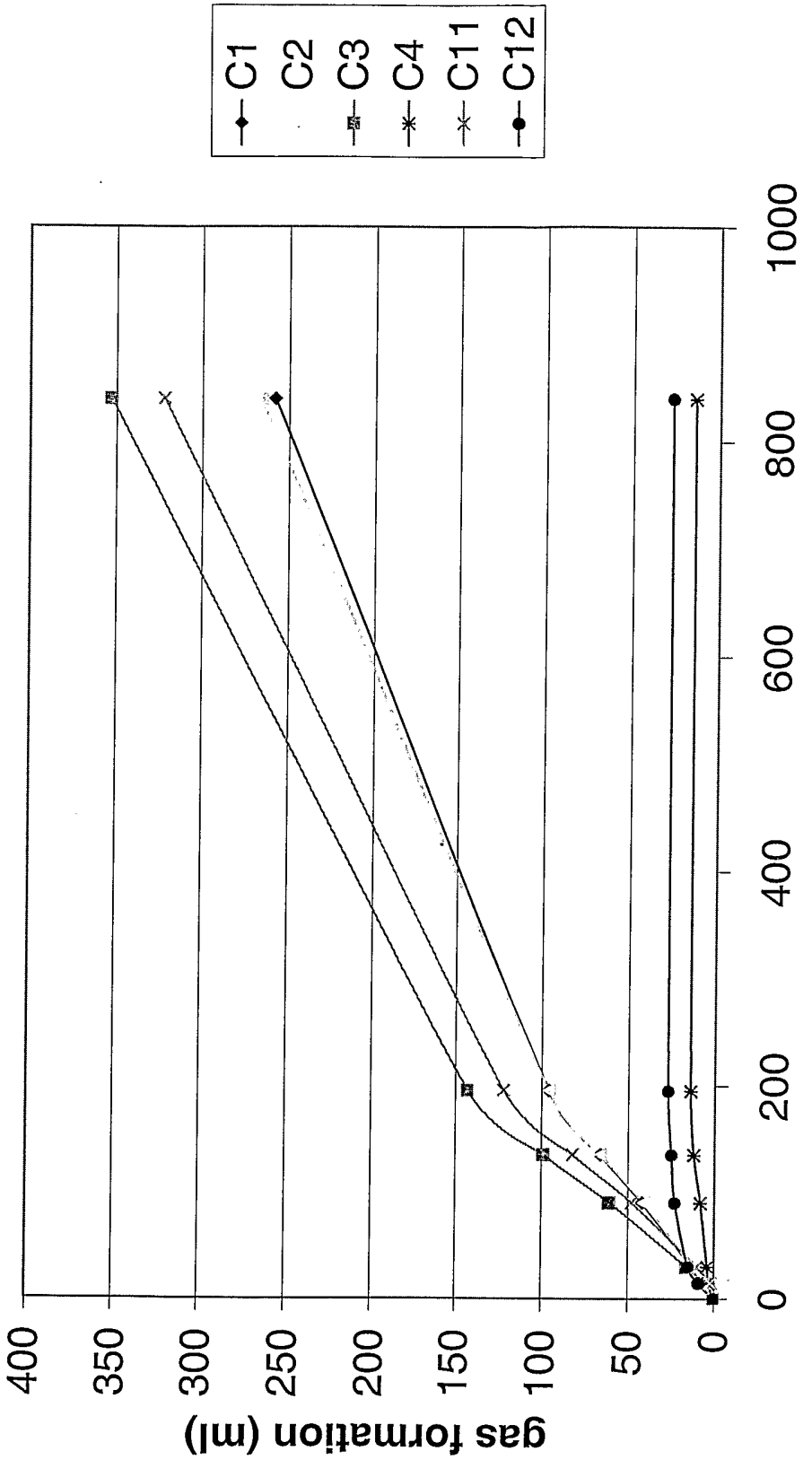
C1
C2
C3
C4
C11
C12
gas formation (ml)
0
50
100
150
200
250
300
350
400
0
200
400
600
800
1000
minutes

Fig. 2

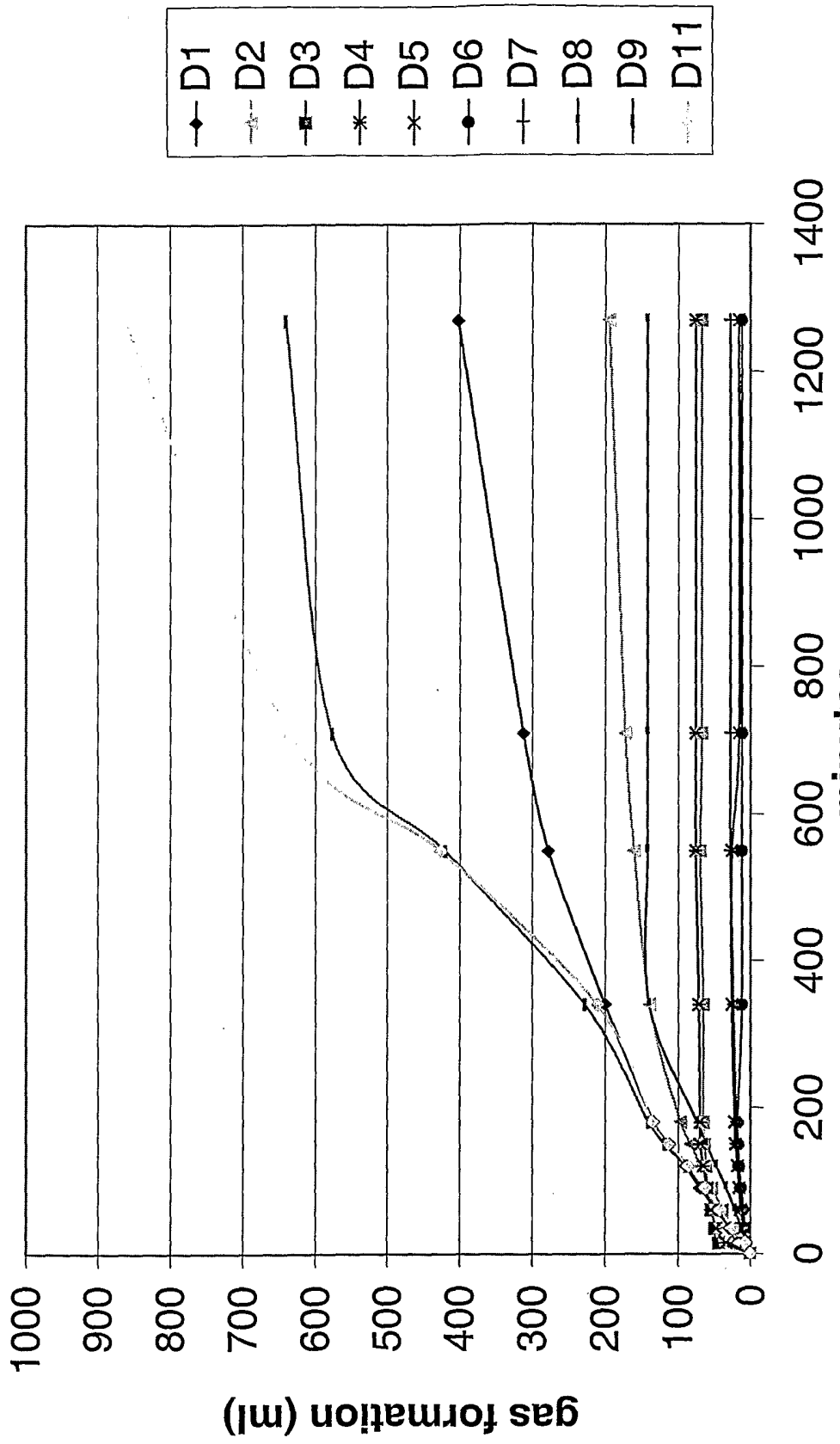
D1
D2
D3
D4
D5
D6
D7
D8
D9
D11
gas formation (ml)
1000
900
800
700
600
500
400
300
200
100
0
0
200
400
600
800
1000
1200
1400
minutes

Fig. 3

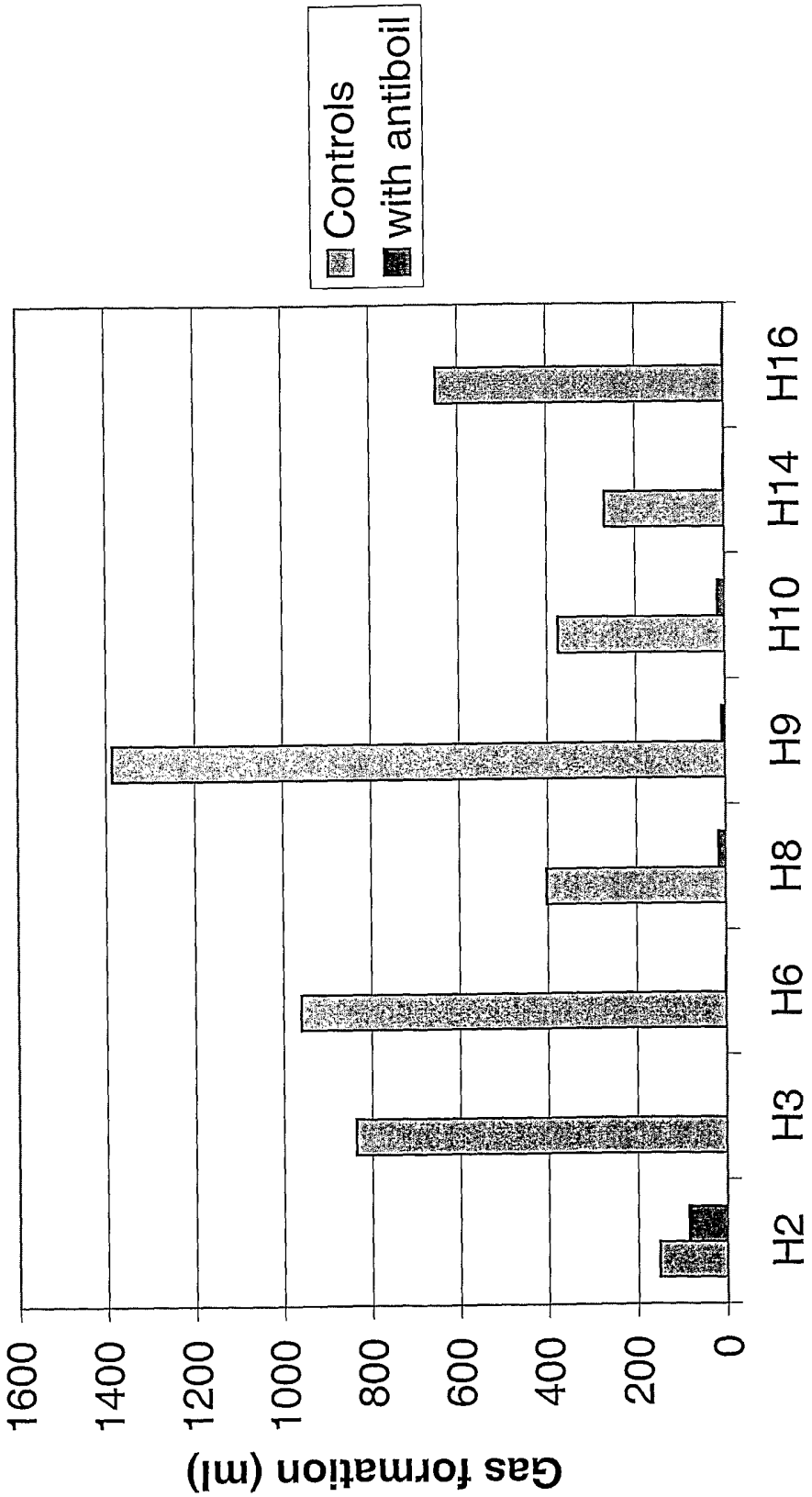
Controls
with antiboil
Gas formation (ml)
1600
1400
1200
1000
800
600
400
200
0
H2
H3
H6
H8
H9
H10
H14
H16
Samples reported to "boil"

Fig. 4

INTERNATIONAL SEARCH REPORT

International application No.
PCT/NO 2003/000303

A. CLASSIFICATION OF SUBJECT MATTER

IPC7: A23K 1/10, A23K 3/00
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7: A23K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI DATA

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 0106869 A1 (HORDAFÖR AS), 1 February 2001 (01.02.2001), claim 12 --	1-5
A	US 4751089 A (MATTI HEIKONEN ET AL), 14 June 1988 (14.06.1988), column 1, line 35 - line 37 --	1-5
A	US 4851240 A (CAROL A. DAY ET AL), 25 July 1989 (25.07.1989), column 2, line 10 - line 15 -- -------	1-5

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:
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Date of the actual completion of the international search	Date of mailing of the international search report
31 March 2004	01-04-2004
Name and mailing address of the ISA/ Swedish Patent Office Box 5055, S-102 42 STOCKHOLM Facsimile No. +46 8 666 02 86	Authorized officer Inger Löfgren/Els Telephone No. +46 8 782 25 00

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CORRECTED

INTERNATIONAL SEARCH REPORT

Information on patent family members

06/09/03

International application No.
PCT/NO 03/00303

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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