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Datasheet for the decision of 24 January 2013

Case Number: T 1552/10 - 3.3.05

Application Number: 02701486.9

Publication Number: 1373135

IPC: C01B 11/20, C02F 1/76

Language of the proceedings: EN

Title of invention:
Stabilised hypobromous acid solutions

Applicant:
MILBRIDGE INVESTMENTS (PTY) LTD

Opponent:
-

Headword:
Hypobromous acid/MILBRIDGE INVESTMENTS

Relevant legal provisions:
EPC Art. 54, 56

Keyword:
"Novelty - (yes)"
"Inventive step - main request (yes) - evidence for improvement - problem plausibly solved over the whole scope of the claims - technical solution not derivable from the prior art"

Decisions cited:
-

Catchword:
-

Case Number: T 1552/10 - 3.3.05

DECISION
of the Technical Board of Appeal 3.3.05
of 24 January 2013

Appellant:
(Applicant)

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Decision under appeal:

Decision of the Examining Division of the European Patent Office posted 10 February 2010 refusing European patent application No. 02701486.9 pursuant to Article 97(2) EPC.

Composition of the Board:

Chairman: G. Raths
Members: H. Engl
D. Prietzel-Funk

Summary of Facts and Submissions

I. This appeal is from the decision of the examining division, posted on 10 February 2010, refusing European patent application EP 02 701 486.9.

II. The documents cited during the examination procedure were:

D1: US-A-5 942 126
D2: US-A-5 422 126
D3: EP-A-0 311 954
D4: Kirk-Othmer, "*Encyclopedia of Chemical Technology*", James Robinson and Betz Dearborn, "*Water, Industrial Water Treatment*", online article posted 4 December 2000, (URL: http://www.mrw.interscience.wiley.com/kirk/articles/indurobi.a01/frame.html), paragraph 14.2
D5: Kirk-Othmer, "*Encyclopedia of Chemical Technology*", John Wojtowicz: "Water, Treatment of Swimming Pools, Spas, and Hot Tubs", online article posted 4 December 2000 (URL: http://www.mrw.interscience.wiley.com/kirk/articles/treawojt.a01/sect1_2-fs.html), paragraph 02.6, table 2.

III. In the contested decision, the subject-matter of claims 1 to 5 of the main request was considered not to involve an inventive step having regard to documents D1 and D3 (Article 56 EPC).

The claims in accordance with the first and second auxiliary requests were regarded as meeting the requirements of the EPC. However, the applicant had previously said it did not agree to the grant of a patent in any version other than the main request. Therefore, the application was refused.

IV. The notice of appeal of the applicant (henceforth: the appellant) was filed by letter dated 9 April 2010. The statement of grounds of appeal was received under cover of a letter dated 18 June 2010 and was accompanied by a set of claims constituting a main request and first and second auxiliary requests.

The following new experimental evidence was also filed:

Annex A: Experimental comparison between the product "Aqua-treat 300" (made according to the application under appeal) and a Nalco product prepared according to D1; and

Annex B: A summary of bromine stability trials conducted in 2009.

V. The independent claims of the main request read as follows:

"1. A method for preparing a stabilised stock hypobromous acid solution including the following steps:

1. preparing a hypochlorous acid solution with a pH of less than 7.5;
2. preparing a bromide solution with a pH of less than 7.0;
3. mixing the hypochlorous acid solution with the bromide solution to form a hypobromous

acid solution; and

4. immediately adding a stabiliser to the solution to provide a stabilised stock hypobromous acid solution with a pH of from 8 to 9."

"7. A stabilised stock hypobromous acid solution having a hypobromous acid concentration of less than 30%(m/m) and containing an amount of cyanuric acid as a stabiliser not exceeding 1 ppm, and wherein the stabilised stock hypobromous acid solution has a pH of 8 to 9."

"25. A method of treating water by adding a stabilised stock hypobromous acid solution as defined in any one of claims 7 to 24 to the water."

The dependent claims define preferred embodiments of the methods of claims 1 or 25 or of the product of claim 7.

VI. The board gave a preliminary opinion of patentability having in particular regard to documents D1 and D2.

The appellant's reply, under cover of a letter dated 15 January 2013, contained new arguments and new claims in accordance with first to fourth auxiliary requests, replacing in part the claims previously on file.

VII. The arguments of the appellant may be summarised as follows:

D1 disclosed a method for preparing a stabilised sodium hypobromite solution by mixing an aqueous solution of alkali or alkaline earth metal hypochlorite with a water-soluble bromide ion source. The pH of the stabilised aqueous alkali or alkaline earth metal hypobromite solution was from about 8 to 11, more preferably from 11 to 14. The hypobromite solution prepared by the method of D1 was a different chemical entity to the stabilised hypobromous acid solution of the application under appeal. Thus, D1 related to a different technical problem.

Having regard to D1, the objective technical problem addressed by the application in suit was to provide a stabilised hypobromous acid solution that was suitable for the treatment or disinfection of water, especially drinking and irrigation water.

In the method of the invention, the bromide solution as claimed in claim 1 had a pH of less than 7, *i.e.* the bromide ion solution was acidified. This meant that the reaction of Br^- with HOCl took place below the pKa (7.5) of HOCl from which it otherwise would be driven upwards, to a more basic pH. At the pH of 8 to 9 of the HOBr solution of the application under appeal, biocidal activity and stability of the solution were optimally combined. Nothing in D1 taught towards the method of claim 1.

Test results filed as Annex A demonstrated that the HOBr solution of the invention, stabilised with cyanuric acid, was unexpectedly more stable for at least three weeks, compared with the products obtained in accordance with D1.

With respect to D2, the appellant argued that said document related to a method for the simple production of reliably defined HOBr solutions having a high concentration of the oxidant. The method comprised the addition of a strongly alkaline solution of bleach to an acidic aqueous solution of HBr in order to oxidise the HBr to an aqueous solution of HOBr with a pH of 6 to 8. The process was based on the discovery that absorbance or colour change could be used to determine when a solution had been produced with well-defined, high concentrations of HOBr. The solutions could be modified by addition of dimethylhydantoin (DMH) and could then be stored for, at best, up to 5 days. The skilled person would thus understand from D2 that only a modest shelf life could be achieved, even when an excess of DMH was added (see example 8). Based on D2, the skilled person would find no motivation to modify the one-step process described therein, where the bleach was neutralised in situ by HBr, with a two-step procedure wherein the bleach was neutralised beforehand in a separate step to form hypochlorous acid. Moreover, the claimed invention provided the unexpected advantage of an extended shelf life of up to 6 months, when stabilised with low concentrations not exceeding 1 ppm of cyanuric acid (see claim 7). There was no teaching in either D1 or D2 to that effect.

D3 related to a method for preventing the decomposition of phosphonates present in cooling waters which also contained as a biocide a combination of chlorine and a bromine salt. D3 did not teach or suggest a method of manufacturing a stabilised stock hypobromous acid.

The method defined in claim 1 was not limited to the use of any particular stabiliser, nor was it limited to the use of a specific amount of stabiliser. Suitable stabilisers would be familiar to the skilled person and included those listed in D1 (column 8, line 62 to column 9, line 5). In a series of experiments, filed as Annex B, it was demonstrated that the addition of either 0.3 ppm of sulfamic acid or 0.3 ppm of boric acid to the solution gave comparable results to the addition of 0.3 ppm of cyanuric acid, as measured by the amount of bromine present after 2 and 7 days. Other experiments presented in Annex B showed that good stability could be achieved irrespective of the amount of stabiliser added.

The appellant submitted that, in the light of this experimental evidence, claim 1 of the main request satisfied the requirement of inventive step across its full breadth and that limiting the claim to a specific stabiliser in the amount specified in claim 5 would be unduly limiting on the appellant, taking into consideration their contribution to the art.

Further arguments concerned the claims in accordance with the first and second auxiliary requests.

VIII. Requests

The appellant requested that the decision under appeal be set aside and that a patent be granted on the basis of claims 1 to 35 of the main request filed with the statement of grounds of appeal or, in the alternative, on the basis of the claims of the first to fourth auxiliary requests filed with letter dated 15 January 2013.

Reasons for the Decision

1. Amendments (Article 123(2) EPC) (main request)

Claim 1 is identical to claim 1 as originally filed. Claim 7 is based on a combination of claims 7 and 10 as originally filed. Claim 25 is based on claim 26 as originally filed, with the back reference adapted.

The dependent claims are also based word-for-word on the corresponding claims as originally filed.

The requirements of Article 123(2) EPC are thus met.

2. Novelty (main request)

2.1 D1 (the Nalco patent) discloses a method of making a stabilised stock hypobromous acid solution by mixing an aqueous solution of alkali or alkaline earth metal hypochlorite with a water-soluble bromide ion source so as to form an unstabilised aqueous solution of alkali or alkaline earth metal hypobromite, and adding a suitable stabiliser and recovering the resultant stabilised aqueous alkali or alkaline earth metal hypobromite solution (see abstract; column 4, lines 18 to 36).

The bromide ion source is preferably NaBr, KBr, LiBr or HBr (see column 5, lines 22 to 24). The preferred stabiliser is an alkali metal sulfamate (see examples 1 and 4); preferred alternative stabiliser are, for instance, urea, thiurea, creatinine, cyanuric acid and alkyl hydantoins (see column 8, line 60 to column 9, line 5). A preferred source of hypochlorite ion is bleach (NaOCl) (see example 6).

The pH of the stabilised alkali or alkaline earth metal hypobromite solution is from about 8 to 14, more preferably from about 11 to 14 (see column 5, lines 37 to 39).

2.2 The method of claim 1 of the application under appeal differs from D1 in that the pH of the hypochlorous acid solution which is mixed with the bromide ion solution is below 7.5, whereas the alkali hypochlorite solution or bleach used in D1 typically has a pH in the vicinity of pH 14 (see application under appeal, page 14, last line). This opinion is shared by the examining division in the contested decision (see Reasons, point 1.2).

The subject-matter of claim 1 and of dependent claims 2 to 6 is therefore novel over D1.

2.3 The appellant submitted that, as a further distinction, D1 did not disclose the preparation of a hypobromous acid solution, but of a hypobromite solution. The board cannot accept this argument because at the lowest pH value disclosed in D1 (pH = 8) the alkali or alkaline earth metal hypobromite solution *de facto* contains mostly undissociated HOBr (pKa of HOBr = 8.8), that is, hypobromous acid.

2.4 The subject-matter of claim 7 is novel having regard to D1 because said document does not directly and unambiguously disclose a stabilised stock hypobromous acid solution of pH of 8 to 9 which is stabilised with cyanuric acid in an amount of less than 1 ppm. Although

D1 discloses a list of potential stabilisers, among them cyanuric acid, there is no concrete disclosure of a hypobromous acid solution having a pH of 8 to 9 which is stabilised with cyanuric acid. The preferred pH range of the stabilised stock hypobromous acid solution according to D1 is much higher, in the range of 11 to 14. D1 also does not disclose the amount of the stabiliser recited in claim 7.

The subject-matter of claim 7 and of method claim 25 referring back to claim 7, is therefore novel over D1.

2.5 D2 discloses a method for the simple and reliable production of HOBr solutions having a high concentration of the oxidant. The method comprises the addition of a strongly alkaline solution of bleach (NaOCl) to an acidic aqueous solution of HBr in order to oxidise the HBr to obtain an aqueous solution of HOBr with a pH of 6 to 8. The process involves the detection of an absorbance or colour change to determine when a solution has been produced with well-defined, high concentrations of HOBr. The solutions may be modified by addition of dimethylhydantoin (DMH) and may then be stored for up to 5 days (see document D2, column, 3, lines 26 to 31; column 4, lines 2 to 6 and 50 to 68; examples 1 and 8; Table 1). The method differs from the one according to claim 1 of the application under appeal in that the OCl^- source (bleach) has a strongly alkaline pH (near 14). The resulting hypobromous acid generally has a neutral pH of 6 to 8 (see column 4, lines 50 to 54); in the examples, a pH of between 6.4 and 7.5 is reported (see examples 1 to 10 and Table 1).

2.6 D3 concerns the use of sulfamic acid to inhibit phosphonate decomposition by chlorine-bromine mixtures. Besides the general formula NaBr + HOCl - > NaCl + HOBr (see page 2, lines 44 to 48), the document is silent on further details of a method for preparing hypobromous acid.

D4 and D5 generally discuss the antimicrobial properties of OBr^- in water treatment; these documents are without special interest regarding the presently claimed methods of making stabilised HOBr solutions, or for the particular stabilised solutions so obtained.

2.7 The subject-matter of the claims of the main request is thus novel and meets the requirements of Article 54 EPC.

3. Inventive step (main request)

3.1 *The claimed invention*

The invention is concerned with a stabilised stock hypobromous acid solution and with a method for preparing it. The application also comprises a method of treating water using this stabilised stock hypobromous acid solution.

3.2 *Closest prior art*

According to the problem-solution approach and established EPO practice, the closest prior art is normally a document intended for the same purpose as the claimed invention and having the most relevant structural features in common.

In this case, two prior-art documents, D1 and D2, could qualify as the closest prior-art document.

D2 concerns a method for producing aqueous solutions of hypobromous acid having a neutral pH of 6 to 8 and high concentrations of the oxidant. A close to quantitative conversion of Br^- to HOBr is obtained (see column 4, lines 50 to 62).

The method of D2 involves reacting an acidic solution of HBr in water with a strongly alkaline solution of household bleach (NaOCl) until a sharp change in absorbance at 400 nm was complete and a neutral pH was reached (see Figure 1). The solutions so obtained may be stabilised with dimethylhydantoin (DMH) which suppresses formation of bromate ions and stabilises the HOBr solution (see Table 1, examples 5, 6, 7, 8 and 10). Alkyl hydantoins are known as stabilisers for HOBr (see D1, column 9, line 1). The solutions of HOBr are used as oxidising biocides for water treatment (column 1, lines 29 to 31).

In view of the background and object of the application under appeal as set out in point 3.1, the examining division considered document D1 to represent the closest prior art, because this document deals with the problem of producing a stabilised solution of hypobromite by a reaction involving the same key reactants.

3.3 *Technical problem*

According to the appellant (see letter dated 18 June 2010, paragraph bridging pages 1 and 2), the technical problem consisted in providing a stabilised stock hypobromous acid solution suitable for the treatment and disinfection of water, especially drinking and irrigation water, and having improved stability.

3.4 *Solution*

As a solution to this technical problem the application proposes a method of preparing a stabilised hypobromous acid solution according to claim 1, including the step of mixing a hypochlorous acid solution with a bromide solution to form a hypobromous acid solution, characterised in that the pH of the hypochlorous acid solution is less than 7.5 (see claim 1, feature 1).

The application also proposes a stabilised stock hypobromous acid solution according to claim 7, having a pH of 8 to 9 and comprising cyanuric acid as a stabiliser in an amount not exceeding 1 ppm.

3.5 *Success of the solution*

The board had to deal with two aspects:

- evidence for the success of the solution; and
- breadth of claim 1.

3.6 Regarding the first aspect, the board relies on the experimental evidence submitted as Annex A (see letter dated 18 June 2010).

According to Annex A, two different solutions of hypobromous acid were prepared, one according to the invention (designated as "Product 1 - Aqua-treat 300"), the other one according to D1 (designated as "Product 2 - Nalco"). The methods of preparation differed in that, in the case of the product according to the invention, the pH-value of the hypochlorite solution was lowered to 7.46 by adding to the sodium hypochlorite solution a 10% solution of HCl, whereas for the prior-art Nalco product the sodium hypchlorite solution was used as it is (pH 12.7) for reacting with the bromide ion solution. Finally, to each hypobromous acid solution 0.3 ppm of cyanuric acid were added as a stabiliser. The final pH of the hypobromous acid prepared according to the invention was 8.67 and the pH of the Nalco product was 11.82.

The subsequent stability test which was carried out over a period of approximately 3 weeks revealed that the product of the invention exhibited a stable Br_2 content of between 13.5% and 13.0% and a stable pH value over the entire period of time. In comparison, the Br_2 content of the Nalco product dropped significantly from initially 56% to 4.9%, accompanied by a slight increase in pH from 11.82 to 11.95. The stability of the product claimed in the application under appeal is therefore distinctly superior.

The board also has no reason to doubt that the claimed product was suitable for the treatment and disinfection of water, especially drinking and irrigation water.

From the experimental evidence discussed above it is thus plausible to the board that the above-defined problem has indeed been successfully solved. This applies both to the method of claim 1 and to the product defined in claim 7.

3.7 *Obviousness*

It remains to be decided whether the claimed solution is obvious having regard to the prior art.

It is true that document D1 discloses a range of pH values from 8 to 14 for the stabilised alkali or alkaline earth metal hypobromite solution, a range which at its lower end overlaps with the pH range of the application under appeal (claiming in claims 1 and 7 a pH range of the stabilised stock hypobromous acid solution of pH 8 to 9). However, the working examples of D1 do not exemplify a pH within that lower end range. The preferred pH range of D1 is from about 11 to 14 (see for instance column 5, lines 37 to 39; column 7, lines 24 to 26; column 8, lines 18 to 20). A hypobromite solution having a low or moderate alkalinity could in theory be obtained by using <u>hydrobromic acid</u> as a source for the bromide ion, thus neutralising the strong alkalinity of the alkali or alkaline earth metal hypochlorite solution. However, hydrobromic acid is not the preferred bromide source of D1. It is mentioned only as one item in a list which includes NaBr, KBr and LiBr, of which NaBr is the preferred Br^- source (see column 5, lines 22 to 28; column 7, lines 10 to 16; column 8, lines 3 to 9). There is no apparent reason why the skilled person should deliberately combine, for instance, a sodium hypochlorite solution with a strongly acidic bromide solution, such as HBr, when the target pH of the final hypobromite solution according to D1 is in the highly alkaline region.

The board concludes that D1 does not suggest preparing a solution of hypobromous acid using hypochlorous acid having a pH of less than 7.5. D1 also does not suggest how to arrive at a stabilised solution of hypobromous acid having a low alkalinity of pH 8 to 9 as claimed in claim 7 of the application under appeal.

As to the teaching of D2, the method according to current claim 1 (main request) differs from the method disclosed in D2 in that the solution of NaOCl having a pH in the vicinity of 14 is replaced by a solution of hypochlorous acid (HOCl) having a pH of less than 7.5. It also differs in that the bleach is neutralised beforehand in a separate step, by adding HCl, not *in situ* as in D2.

The HOBr solutions stabilised with DMH in accordance with the examples provided in D2 exhibit only a moderate shelf life. Some solutions immediately developed a precipitate (examples 5, 7 and 10), others remained colourless without precipitate for 5 days, and there is no disclosure in D2 of a solution which is stable for a prolonged period of time.

In view of the experimental evidence discussed under point 3.5 above, it is plausible that an improvement over D2 (stability in the order of days only; precipitation occurs in many test samples) has also been achieved.

D2 discloses HOBr solutions which tend to form precipitates and possess only a comparatively short shelf life, even when an excess of DMH is added as a stabiliser (as in example 8). The skilled person would find no motivation in D2 to modify the one-step process described therein, where the bleach is neutralised *in situ* by HBr, with a two-step procedure wherein the bleach is neutralised beforehand in a separate step to form hypochlorous acid, in order to improve the stability of the HOBr solutions.

Indeed, as discussed earlier, the presently claimed invention provides the unexpected advantage of an extended shelf life of up to 6 months, when stabilised with low concentrations not exceeding 1 ppm of cyanuric acid. Although stabilisation with cyanuric acid is generally known from D1 (column 8, line 67) and D4 (section 2.7), there is no teaching in D1, D2 or D4 of the low effective amounts used in the present invention.

Starting from D2 as the closest prior art and considering the hints in D1 which could lead the skilled person to the claimed solution, the reasoning would be just the reverse.

3.8 The board now turns to the issue of the breadth of claim 1, in particular the question of whether the method of claim 1 according to the main request should be limited to the use of cyanuric acid as a stabiliser.

The board firstly observes that a variety of suitable stabilisers besides cyanuric acid is known from D1 (column 8, line 62 to column 9, line 5). Sulfamic acid as a stabiliser is disclosed *inter alia* in D3.

However, the appellant demonstrated (see the experimental evidence filed as Annex B and attached to the letter dated 18 June 2010) that the addition of amounts of either 0.3 ppm of sulfamic acid or of 0.3 ppm of boric acid as a stabiliser to the solution of hypobromous acid gave results comparable to the addition of 0.3 ppm of cyanuric acid, as determined by the amount of bromine present after 2 and 7 days. The experiments showed that good stability could be achieved with amounts of stabiliser of 0.3 ppm and 2 ppm. Every tested stabiliser performed better than the control sample (without stabiliser).

The board is thus satisfied that the problem underlying the application under appeal (as defined above) is indeed solved irrespective of the particular choice of the stabiliser and its specific amount.

3.9 The subject-matter of claims 1 and 7, and of claim 25 referring back to claim 7, thus involves an inventive step.

3.10 In conclusion, the subject-matter of claims 1, 7 and 25 is novel and involves an inventive step. The dependent claims define preferred embodiments of the methods of claims 1 or 25 or of the product of claim 7 and are thus likewise patentable.

3.11 Since the main request can be allowed, there is no need to consider the auxiliary requests.

Order

For these reasons it is decided that:

1. The decision under appeal is set aside.

2. The case is remitted to the department of first instance with the order to grant a patent on the basis of the claims according to the main request, filed with the statement of grounds of appeal, and a description and drawings to be adapted.

The Registrar	The Chairman
C. Vodz	G. Raths