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**D E C I S I O N**  
**of 21 December 1999**

**Case Number:** T 0607/95 - 3.3.5

**Application Number:** 92201955.9

**Publication Number:** 0522634

**IPC:** C01B 21/14

**Language of the proceedings:** EN

**Title of invention:**

Direct catalytic process for the production of hydroxylamine

**Applicant:**

Enichem S.p.A.

**Opponent:**

-

**Headword:**

Production of hydroxylamine/ENICHEM

**Relevant legal provisions:**

EPC Art. 54, 56

**Keyword:**

"Novelty (yes)"  
"Inventive step (yes)"

**Decisions cited:**

-

**Catchword:**

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Boards of Appeal

Chambres de recours

**Case Number:** T 0607/95 - 3.3.5

**D E C I S I O N**  
**of the Technical Board of Appeal 3.3.5**  
**of 21 December 1999**

**Appellant:** Enichem S.p.A.  
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**Representative:** Fusina, Gerolamo  
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**Decision under appeal:** Decision of the Examining Division of the  
European Patent Office posted 16 March 1995  
refusing European patent application  
No. 92 201 955.9 pursuant to Article 97(1) EPC.

**Composition of the Board:**

**Chairman:** R. K. Spangenberg  
**Members:** M. M. Eberhard  
M. B. Günzel

## Summary of Facts and Submissions

- I. European patent application No. 92 201 955.9 claiming the priority date of 10 July 1991, was refused by a decision of the examining division. The decision was based on amended claims 1 to 13 filed with the appellant's letter dated 17 December 1993 with the additional amendments in claim 1 requested in the letter of 12 May 1994. These claims concern a catalytic process for the production of hydroxylamine by oxidation of ammonia with hydrogen peroxide.
- II. The ground for the refusal was that the subject-matter of amended claim 1 lacked novelty over the disclosure of EP-A-0 208 311 (hereinafter D1). According to the decision, although D1 concerned the production of cyclohexanone-oxime, the footnote on page 4 disclosed that nitrogen protoxide (ie nitrous oxide  $N_2O$ ) was formed by decomposition of hydroxylamine, which was a by-product of the process. Therefore, hydroxylamine was produced at some point in the process of D1. Hydroxylamine being a polar compound, it was very likely that a major part thereof would stay in the aqueous liquid phase, where it was formed. The passage of D1 referring to the decomposition of hydroxylamine was not to be interpreted as necessarily implying that all the hydroxylamine was decomposed. This was enough to deprive the subject-matter of claim 1 of novelty, even though cyclohexanone-oxime, and not hydroxylamine, was the desired product in D1.
- III. The appellant lodged an appeal against this decision. In reply to a communication of the board of appeal, two sets of amended claims were filed with the appellant's

letter dated 18 May 1999, as a main request and an auxiliary request. With his letter dated 23 August 1999, the appellant submitted a set of amended claims, as a main request in replacement of the previous one, as well as amended pages of the description. Claim 1 of the main request reads as follows:

"1. Direct catalytic process for the production of hydroxylamine, by means of the oxidation of ammonia with hydrogen peroxide, in an organic solvent, water or a mixture of water and an organic solvent, wherein the catalyst is composed of silicon, titanium and oxygen and the structure of said catalyst is crystalline or amorphous."

- IV. Concerning the novelty issue, the appellant argued that according to the authors of D1 the side reaction producing hydroxylamine in D1 was the hydrolysis of the cyclohexanone-oxime. A decomposition reaction, favoured by alkalis, would then have given the nitrous oxide  $N_2O$ . This hypothesis was made in order to explain the small amount of  $N_2O$  in the gas phase and found support in citations illustrating the common general knowledge at the date of D1, such as ref. 1 (Kirk-Othmer Encyclopaedia of Chemical Technology, second edition, vol. 11 (1966), pages 493 to 508), ref. 2 (Organic Chemistry, A. R. Day and M. M. Joullié, 1960, pages 330 to 331) and ref. 3 (Organic Chemistry, J. B. Hendrickson, D. J. Cram, G. S. Hammond, 1970, pages 468 to 471). Another hypothesis concerning the formation of  $N_2O$  could be based on the oxidative deoxygenation of cyclohexanone-oxime. The appellant further argued that cyclohexanone was not quantitatively converted to the oxime in D1 and that

the cyclohexanone would have quantitatively reacted with hydroxylamine if the latter had been present in the liquid phase, as shown by ref. 2 and ref. 3. It was not disclosed in the cited references that the formed hydroxylamine could derive from the direct oxidation of ammonia with hydrogen peroxide. The appellant also put forward arguments in favour of an inventive step with respect to D1 and D2 (EP-A-0 314 147).

- V. The appellant requested that the decision of the examining division be set aside and that a patent be granted with amended claims 1 to 13 submitted with the letter dated 23 August 1999 and the amended description filed at the same date. As an auxiliary request, the appellant requested that a patent be granted on the basis of the amended claim according to the auxiliary request submitted with the letter of 18 May 1999.

### **Reasons for the Decision**

1. The appeal is admissible.
  
2. Amended claims 1 to 13 of the main request meet the requirements of Article 123(2) EPC. In particular it is directly and unambiguously derivable from the paragraph bridging pages 2 and 3 of the description as filed and from original claim 6 that the catalytic process is carried out in an organic solvent, water, or a mixture of water and an organic solvent. The features indicated in dependent claims 2 to 13 are disclosed in the original claims 2 to 13. The amendments in the description also fulfill the requirements of Article 123(2) EPC.

3. D1 discloses a catalytic process for preparing cyclohexanone-oxime by reacting cyclohexanone with ammonia and hydrogen peroxide in the liquid phase in the presence of a catalyst such as a titanium silicalite, optionally in admixture with an inert binder (see claims 1 and 2; column 1, lines 14 to 22). Data concerning the operating conditions and the results obtained in Examples 1 to 4 are reported in Table 1 which also indicates the composition of the gas phase. According to the footnote below Table 1, "nitrogen protoxide derives from the decomposition of hydroxylamine, which forms in consequence of a parallel reaction".

D1 does not concern the preparation of hydroxylamine but the preparation of cyclohexanone-oxime. However, taking into account that hydroxylamine was formed in a side reaction, the question arises whether or not it can be directly and unambiguously derived from this teaching that hydroxylamine can be prepared by the direct catalytic oxidation of ammonia with hydrogen peroxide.

D1 itself neither gives the composition of the liquid phase nor discloses which side reaction leads to the formation of hydroxylamine. Furthermore, it is not indicated in D1 that some hydroxylamine is still present in the liquid phase of the examples. Therefore, only assumptions can be made as to how hydroxylamine was produced, whether or not the whole amount of hydroxylamine would be subsequently decomposed, and if not, whether the undecomposed hydroxylamine would be present in the liquid phase or would have reacted with other compounds thereof. The Appellant has argued that,

according to the authors of D1, the side reaction producing hydroxylamine, referred to in D1, was the hydrolysis of cyclohexanone-oxime which leads to cyclohexanone and hydroxylamine and can occur under the ammoximation conditions used in the examples of D1. According to the appellant, only small amounts of hydroxylamine would be expected to form under the experimental conditions used in D1 since the equilibrium constant favours the oxime formation. A decomposition of the hydroxylamine enhanced by alkali would subsequently occur and explain the presence of N<sub>2</sub>O in the gas phase. These arguments were supported by the disclosure in citations illustrating common general knowledge, ie ref. 1, page 496; ref. 2, page 331; ref. 3, page 470. The board observes that if these assumptions were correct, then the hydroxylamine formed in the side reaction would not result from the direct catalytic oxidation of ammonia with hydrogen peroxide but from the hydrolysis of cyclohexanone-oxime, ie from a process different from the claimed one. Furthermore, the ammoximation of cyclohexanone takes place in the presence of a titanium silicalite in a reaction medium comprising ammonia, hydrogen peroxide, cyclohexanone and water, and the mechanism of ammoximation over this catalyst is not disclosed in D1. There is also no evidence in the file that this mechanism was known at the relevant date of D1. According to D3 (Journal of Molecular Catalysis, 69, (1991), pages 383 to 392, published after the priority date of the present application and cited in the search report), reports on the mechanism of the reaction disclosed in D1 were still not available in 1991 (see D3, page 384, first paragraph of the chapter "results and discussion"). In these circumstances, it is not clear to the board on

which basis the skilled person would directly and unambiguously derive from D1 that hydroxylamine was formed by the direct oxidation of ammonia with hydrogen peroxide.

Furthermore, D1 teaches that  $N_2O$  derives from the decomposition of hydroxylamine. In the decision appealed, it was assumed that the hydroxylamine formed in a side reaction would not be entirely decomposed and that a part thereof would remain in the liquid phase. However, this is not directly and unambiguously derivable from D1. In the board's view, the polar character of hydroxylamine is not sufficient to support this assumption since the question whether or not a part of the hydroxylamine remains in the liquid phase also depends on the conditions of the ammoximation reaction and on the products contained in the reaction medium. It is disclosed in D1 that unreacted cyclohexanone is still present in the final liquid phase (see column 3, lines 1 to 5 and the conversion of cyclohexanone in Table 1). As pointed out by the appellant, assuming that a small amount of hydroxylamine was not decomposed, then the skilled person would not expect this hydroxylamine to remain in the liquid phase but to react with the unconverted cyclohexanone still present therein. For the preceding reasons the board is not convinced that it would be directly and unambiguously derivable from the disclosure of D1 that hydroxylamine can be produced by the direct catalytic oxidation of ammonia with hydrogen peroxide in the presence of titanium-silicalite as the catalyst. Therefore, the process for preparing cyclohexanone-oxime disclosed in D1 is not considered as destroying the novelty of the claimed process and



the subject-matter of claim 1 meets the requirement of novelty over the disclosure of D1.

The process according to claim 1 of the main request is also novel with respect to D2 and EP-A-0 347 926 (hereinafter D4) cited in the search report. D3 was published between the priority date and the filing date of the present application. As the priority date can be accorded to claim 1, D3 does not form part of the state of the art with respect to claim 1.

4. None of the documents cited in the search report concerns the preparation of hydroxylamine. Therefore, none of them can be considered to represent the closest state of the art.

According to the present application (page 1, line 6 to page 2, line 7), the various processes which have been carried out so far to produce hydroxylamine are based on the reduction to hydroxylammonium salts, of derivatives of nitrogen at a higher oxidation state, such as nitrogen oxides, nitrites or nitrates. This reduction can take place by means of catalytic hydrogenation. One of the disadvantages of such processes is the risk of formation of explosive mixture  $N_2O+H_2$  and also the necessity of regenerating the catalyst by a labourious process. Furthermore, the coproduction of ammonium salts is inevitable, both in the reduction stage and subsequently during the production of solutions of free hydroxylamine in water or in alcohol. Starting from this prior art, the problem underlying the patent application can be seen in the provision of another process for the production of hydroxylamine.

It is proposed that this problem be solved by the direct catalytic oxidation of ammonia with hydrogen peroxide, in an organic solvent, water or a mixture of water and an organic solvent, in the presence of a catalyst as defined in claim 1. In view of the yields of hydroxylamine obtained in the examples of the description, the board is satisfied that the problem has actually been solved by the claimed process.

- 4.1 As indicated above, D1 does not concern the production of hydroxylamine but the preparation of cyclohexanone-oxime by reaction of cyclohexanone with ammonia and hydrogen peroxide in the presence of titanium silicalite as a catalyst. Already for this reason, the board doubts that the skilled person confronted with the problem stated above, namely the production of hydroxylamine, would have considered this document as being of interest. Even if the skilled person had paid attention to D1, this document would have been of no assistance to him since the sole information about the possible formation of hydroxylamine is that given in the footnote on page 5, which teaches that hydroxylamine formed in a side reaction **is decomposed**. The skilled person would not have relied on a process which leads to the decomposition of the product he wants to obtain. Furthermore, as already pointed out above, D1 does not disclose which side reaction was assumed to give some hydroxylamine during the ammoximation process nor does it mention the mechanism of the ammoximation reaction over titanium silicalite. Therefore, the disclosure in the said footnote could not have suggested to the skilled person that hydroxylamine can be produced in a reasonable yield by direct catalytic oxidation of ammonia with hydrogen

peroxide in an organic solvent, water, or a mixture thereof, in the presence of a catalyst as defined in claim 1, in particular a titanium silicalite.

- 4.2 D2 discloses a process for the synthesis of N,N-dialkyl-hydroxylamines by reaction of the corresponding secondary dialkylamines with hydrogen peroxide in the presence of a catalyst based on titanium-silicalite (see claim 1). In Example 1, N,N-diethylhydroxylamine is prepared by reaction of diethylamine with hydrogen peroxide in the presence of a titanium silicalite in t-butyl alcohol. In the board's view, the skilled person could not have expected, in view of this teaching, that hydroxylamine might be obtained in a reasonable yield by the direct oxidation of ammonia with hydrogen peroxide in the presence of titanium-silicalite since he was aware of the much higher reactivity of ammonia compared to diethylamine. As emphasised by the appellant, in the case of the synthesis of N,N-diethylhydroxylamine the **single hydrogen atom** bound to the nitrogen atom of diethylamine has to undergo oxidation in order to obtain the desired product, whereas the preparation of hydroxylamine by direct catalytic oxidation of ammonia with hydrogen peroxide would require the oxidation of **only one of the three available** hydrogen atoms.

- 4.3 D4 does not concern the preparation of hydroxylamine but a catalytic process for the manufacture of oximes by ammoximation of the corresponding carbonyl compounds. It contains no information which could point towards the claimed process, even when considered in combination with the teaching of D1 and D2.

It follows from the above that the subject-matter of claim 1 according to the main request also meets the requirement of inventive step set out in Articles 52(1) and 56 EPC.

5. Claim 1 being allowable, the same applies to dependent claims 2, 4 and 7 to 9 to which the priority date can also be accorded and whose patentability is thus supported by that of claim 1.
  
6. Dependent claims 3, 5, 6 and 10 to 13, contain some features which are not disclosed in the priority document (titanium-silicalite of type 2 in claim 3; ammonia fed in the form of gas in claim 5; the higher concentration of the solution of hydrogen peroxide in claim 6; the whole features of claim 10; the higher mole ratios of ammonia:hydrogen peroxide in claim 11; the "isothermal" reactor in claims 12 and 13). The board observes that in view of the point of law concerning the interpretation of the expression "the same invention" in Article 87(1) EPC, which was referred to the Enlarged Board of appeal under the file number G 2/98 (see OJ EPO, 1998, 509 to 510), it might be questionable whether the priority date can be accorded to these dependent claims. However, this question can remain open, since even if the priority date were not valid for these claims and D3, thus, formed part of the state of the art, the subject-matter of these claims would be considered to meet the requirements of patentability with respect to the cited prior art including D3.
  - 6.1 D3 concerns the ammoximation of cyclohexanone over a titanium silicate molecular sieve, TS-2. It reports the

catalytic activity and selectivity of this catalyst and other catalysts in the ammoximation of cyclohexanone and other carbonyl compounds with ammonia and hydrogen peroxide. Mechanisms for the formation of cyclohexanone-oxime and peroxy-dicyclohexyl amine are proposed on the basis of the studies carried out at different temperatures and reactant concentrations (see page 383, abstract; pages 390 to 391). The first mechanism of reaction proposed on page 390 comprises a step in which a peroxytitanio complex would react with  $\text{NH}_3$  to form hydroxylamine which would thus react with cyclohexanone to form cyclohexanone-oxime. The second mechanism proposed in D3 comprises the formation of cyclohexylimine as the intermediate product. However, D3 teaches on page 391 that the second mechanism, contrary to the first one, also explains the formation of the major by-product, ie peroxy-dicyclohexyl amine. Therefore, the second mechanism would be considered by the skilled person as the most plausible one. Furthermore, in the hypothetical first mechanism of reaction the hydroxylamine which is supposed to be formed would immediately react with the cyclohexanone of the reaction medium to form the desired cyclohexanone-oxime. Therefore, the hypothetical first mechanism of reaction disclosed in D3 does not destroy the novelty of the process of production of hydroxylamine by direct catalytic oxidation of ammonia with hydrogen peroxide as defined in dependent claims 3, 5, 6 and 10 to 13.

- 6.2 Regarding inventive step, the board's considerations in points 4 to 4.3 above apply likewise to dependent claims 3, 5, 6 and 10 to 13. Furthermore, as D3 does not concern the production of hydroxylamine, but the

oximation of cyclohexanone using ammonia and hydrogen peroxide over a titanium-silicalite, the skilled person confronted with the problem stated above would, a priori, not have paid any particular attention to this document. Even if he had not discarded D3, he would have inferred therefrom that the second mechanism of reaction involving the formation of cyclohexylimine as the intermediate product and not hydroxylamine, is the most plausible or the correct one since it can also explain the formation of the major by-product, contrary to the first hypothetical mechanism (see point 6.1 above). In these circumstances and as D3 contains no further information suggesting that hydroxylamine might be obtained by direct oxidation of ammonia with hydrogen peroxide in the presence of a titanium-silicalite, this document would not have given the skilled person a hint towards the claimed process, even taken in combination with the teaching of D1, D2 and D4. Therefore, the subject-matter of dependent claims 3, 5, 6, and 10 to 13 also fulfills the requirement of inventive step.

**Order**

**For these reasons it is decided that:**

1. The decision under appeal is set aside.
2. The case is remitted to the first instance with the order to grant a patent with claims 1 to 13 according to the main request filed with the letter dated 23 August 1999 and the adapted description (pages 1, 1a, and 2 to 8) filed at the same date.

The Registrar:

The Chairman:

S. Hue

R. Spangenberg