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Boards of Appeal

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(14)

Case Number : T 79/85

DECISION
of the Technical Board of Appeal 3.3.1
of 19 February 1987

Appellant : (Opponent)	BASF Aktiengesellschaft Carl-Bosch-Strasse 38, D-6700 Ludwigshafen
Representative :	
Respondent : (Proprietor of the patent)	Davy McKee (London) Limited 250, Euston Road, London NW1 2PG
Representative :	Eyles, Christopher Thomas Batchellor, Kirk and Eyles 2, Pear Tree Court, Farringdon Road, London EC1R ODS
Decision under appeal :	Decision of Opposition Division of the European Patent Office dated 25 January 1985 rejecting the opposition filed against European patent No. 0 016 286 pursuant to Article 102(2) EPC.

Composition of the Board :

Chairman : K. Jahn
Member : J. Arbouw
Member : P. Ford

Summary of Facts and Submissions

I. European patent No. 16 286 incorporating 10 claims was granted to the Respondents on 6 April 1983 on the basis of European patent application No. 79 302 709.5, filed on 28 November 1979 and claiming a priority of 21 March 1979 (GB-7 910 012).

II. The Appellants filed a reasoned opposition on 25 October 1983 on the basis of new documents, and requested that the patent be revoked in its entirety on the basis of Article 100 EPC.

III. By the decision under appeal of 25 January 1985 the Opposition Division maintained the patent.

The independent Claims 1 and 9 read as follows:

"1. A hydroformylation process for the production of n-valeraldehyde which comprises contacting a C_4-olefin feedstock with carbon monoxide and hydrogen at elevated temperature and at elevated pressure in a hydroformylation zone in the presence of a catalytic quantity of a rhodium complex catalyst comprising rhodium in complex combination with carbon monoxide and a triorganophosphine ligand, in the presence of free triorganophosphine ligand, and recovering n-valeraldehyde from the hydroformylation zone characterised in that the C_4-olefin feedstock comprises butene-1 and at least one other C_4-olefin selected from cis-butene-2, trans-butene-2, and iso-butylene, that the hydroformylation zone contains in excess of 100 moles of free triorganophosphine ligand per gram atom of rhodium and is maintained at a temperature in the range of from 80°C to 130°C, and at a total pressure of not more than 4907 kPa (50 kg/cm^2

absolute), the partial pressure of carbon monoxide being less than 147 kPa (1.5 kg/cm^2 absolute) and the partial pressure of hydrogen being in the range of from 98 to 736 kPa (1.0 to 7.5 kg/cm^2), and that, in addition to n-valeraldehyde, substantially all of said at least one other C_4-olefin is recovered from the hydroformylation zone.

9. A continuous process for the production of n-valeraldehyde by hydroformylation of butene-1 which comprises

   (i) providing a hydroformylation zone containing a liquid charge containing (a) a rhodium complex catalyst wherein rhodium is in complex combination with carbon monoxide and a triorganophosphine, (b) excess triorganophosphine, (c) liquid n-valeraldehyde product, and (d) polymeric aldehyde condensation products;

   (ii) feeding butene-1 to the hydroformylation zone;

   (iii) supplying make up hydrogen and carbon monoxide to the hydroformylation zone;

   (iv) maintaining the hydroformylation zone under hydroformylation conditions;

   (v) recovering from the hydroformylation zone product n-valeraldehyde and unreacted butene-1; and

   (vi) recycling unreacted butene-1 to the hydroformylation zone;

characterised in that butene-1 is supplied to the hydroformylation zone as a liquid C_4-olefin feedstock in admixture with at least one other C_4-olefin selected from cis-butene-2, trans-butene-2, and isobutylene, that the hydroformylation zone contains at least 100 moles of free triorganophosphine per gram atom of rhodium and is maintained at a temperature in the range of from 80°C to 130°C and at a total pressure of not more than 4907 kPa (50 kg/cm^2 absolute), the partial pressure of butene-1 being less than 392 kPa (4.0 kg/cm^2 absolute), the partial pressure of carbon monoxide being less than 147 kPa (1.5 kg/cm^2 absolute), and the partial pressure of hydrogen being from 98 to 736 kPa (1.0 to 7.5 kg/cm^2 absolute), that a liquid reaction product is recovered from the hydroformylation zone and has its pressure reduced, unreacted C_4-olefins and product n-valeraldehyde thereafter being flashed into the vapour phase from the liquid reaction product, that the resulting liquid reaction residue, now depleted in C_4-olefins and product n-valeraldehyde, is recycled to the hydroformylation zone, and that product n-valeraldehyde and unrected C_4-olefins including substantially all of said at least one other C_4-olefin are condensed from the vapour phase, unreacted C_4-olefins thereafter being recycled to the hydroformylation zone."

IV. The decision to maintain the patent was based on the finding that its subject-matter is novel with respect to the closest prior art (1) US-A-3 527 809 in that a mixed C_4-olefin feedstock is used and in that an excess of at least 100 moles of triorganophosphine ligand per gram atom of rhodium is used.

As regards inventive step it was decided that (1) does not suggest the selective hydroformylation of a mixed-olefin feedstock since (1) only deals with the hydroformylation of pure alpha-olefins. A combination of the documents (1) and (3), J. Chem. Soc. (A), 1970, pages 2753 to 2754, was not allowable since (3) is directed to the use of a different catalyst. Therefore, the fact that alk-(2)-enes react about 25 times more slowly than alk-(1)-enes could not be combined with the teaching of (1).

V. The Appellants filed a notice of appeal on 7 March 1985 and duly paid the appeal fee. They filed a reasoned Statement of Grounds of the appeal on 14 May 1985. The Respondents filed submissions in answer on 1 October 1985.

VI. The Appellants argue that a combination of the documents (1) and (3) is allowable since both documents use a rhodium-carbon monoxide-triorganophosphine catalyst. Document (1) teaches the skilled man that alpha-olefins under the chosen conditions mainly react to normal aldehydes. The teaching of (3) (see the later cited page 2759) is that alpha-olefins are much more reactive under the hydroformylation conditions than beta-olefins and branched olefins. The process according to the patent is the mere combination of both teachings, whereby the result - a preferred hydroformylation of the butene-1 and a high normal/isovaleraldehyde ratio - can be predicted.

During the appeal proceedings the Appellant introduced additional documents. It was submitted that US-A-3 290 379 (4) and Pruett, Annals New York Academy of Sciences, Volume 295 (1977), pages 239-248 (6) disclose the selectivity of rhodium/triphenyl phosphorus ligand catalyst in the hydroformylation of mixtures of methylbutenes to 4-methyl-valeraldehyde and of octene-1 and octene-2 to n-nonaldehyde.

It was further argued that DE-C-2 064 471 (7) discloses an excess of up to 5 000 moles of ligand per gram atom of rhodium in the catalytic system.

VII. The Respondents submit that the choice of the hydroformylation conditions according to the invention not only results in the selective hydroformylation of butene-1 in a mixed C_4-olefin feedstock, but also to a high normal/iso valeraldehyde ratio. This could not be expected from document (1) or (3) or from the combination thereof. According to the Respondent the man skilled in the art would have expected from the teaching of (3) a significantly higher proportion of iso-valeraldehyde in the hydroformylation product of a mixed C_4-olefin feedstock, and also a small amount of 3-methyl-butyraldehyde, resulting from the hydroformylation of isobutylene. It is surprising that this does not occur under the reaction conditions of the patent.

The Respondents further argue that the reaction conditions of (4) and the catalyst used are different and that therefore the results are not comparable.

VIII. The parties reaffirmed their points of view in the oral proceedings on 19 February 1987. The Appellant mainly based their arguments on documents (3), (6) and (7).

During oral proceedings the Board made the point that US-A-3 965 192 (12) a document cited and acknowledged in the specification appears to be of particular relevance.

IX. The Appellants request that the decision under appeal be set aside and that the patent be revoked.

The Respondents request that the appeal be dismissed and that the patent be maintained as granted.

Reasons for the Decision

1. The appeal complies with Articles 106 to 108 and Rule 64 EPC and is therefore admissible.

2. The closest prior art is still represented by (1). This document is concerned with a process for the hydroformylation of alpha-olefins in the presence of a complex catalyst comprising rhodium in complex combination with carbon monoxide and a triorganophosphorus ligand, to produce aldehydes having a high ratio of normal aldehydes to branched chain aldehydes (see column 1, lines 21-30 and Claim 1). Document (1) mentions inter alia 1-butene as a useful alpha-olefin (see column 4, line 40) and triorganophosphines (e.g. triarylphosphines, see column 3, lines 58-59 and triphenylphosphine, see Claims 5 and 6) as catalyst. Document (1) further discloses a reaction temperature of 50 to 145°C (see column 6, lines 47-58) a total pressure of less than about 450 p.s.i. (3103 kPa) (see column 6, lines 5-12) and the use of excess ligand, whereby a molar ratio of ligand to rhodium of 100:1 appears to be the practical upper limit (see column 5, line 63 to column 6, line 4).

The economy of this known process using butene-1 is adversely affected in that butene-1 has to be separated from the mixture of C_4-olefins which is normally produced in oil refineries.

3. The technical problem underlying the invention with respect to (1) is, therefore, making available a more economic hydroformylation process for the production of valeraldehyde without impairing the high n-valeraldehyde to iso-valeraldehyde ratio.

In order to solve this problem the Patentee proposes the hydroformylation of a mixed C_4-olefin feedstock with carbon monoxide and hydrogen at a temperature in the range of 80-130°C and at a total pressure of not more than 4907 kPa, the partial pressure of carbon monoxide being less than 147 kPa and the partial pressure of hydrogen being in the range of from 98-736 kPa in the presence of a rhodium-carbon monoxide-triorganophosphine complex and free triorganophosphine ligand in excess of 100 moles per mole of rhodium.

The Board is satisfied that the process according to the patent-in-suit solves this technical problem (see Examples 1, 2 and 3, Table 3 compared with Example 1). Since this point was not in dispute, it need not be further considered.

4. Examination of the cited documents has revealed that this technical teaching is not disclosed there. Consequently, the method according to Claim 1 of the patent-in-suit is novel having regard to the prior art. Since novelty was not disputed by the Appellants, it is not necessary to enter into details.

5. It still remains to be examined whether the requirement for inventive step is met by the subject-matter claimed. It was in fact known from (1) that the use of a high ligand to Rh-ratio of at least 2:1 preferably 5:1 with a practical upper limit of 100:1 (see column 5, line 63 to column 6, line 4) positively affects the normal to iso-

ratio in the hydroformylation of alpha olefins including butene-1. However, there is no teaching in (1) as regards the hydroformylation of olefins other than alpha-olefins, e.g. butene-2 or olefins having the double bond at a tertiary carbon atom, e.g. iso-butylene, not to mention the selective hydroformylation of butene-1 in the mixed C_4-olefin feedstock.

5.1 Document (7) describes inter alia the hydroformylation of butene-1 (see page 3, lines 20-25) and indicates as conditions for the hydroformylation reaction a CO to H_2 ratio of 1:2 to 15:1 (claim), a total pressure of 55.2 - 13.8 bar (5500-1380 kPa) (page 3, line 41) a temperature range of 115-140°C (claim) and a catalytic system comprising this (triphenylphosphine) rhodium-carbonyl hydride/triphenylphosphine whereby triphenylphosphine can be used in an excess of 150 to 5000 moles per mole of Rh (see Example 1 and claim).

However, there is no teaching in (7) as regards the selective hydroformylation of butene-1 in a mixture with butene-2 and/or isobutylene. Moreover, in spite of using a very high ligand to Rh ratio (380:1) the ratio between n- and iso-aldehyde is not very impressive (between 4,3:1 and 16:1, see Example 1).

5.2 The Appellants argue that it would have automatically occurred to the skilled person that under the reaction conditions of the patent-in-suit butene-1 in a mixed C_4-olefin feedstock will be selectively hydroformulated to n-valeraldehyde since (6) teaches that by reacting a mixture of octene-1 and octene-2 under similar reaction conditions good yields of the linear aldehyde were obtained whereas octene-2 did not react (see page 242, para. 3 and Scheme 6). However, although it is indicated that a rhodium-triphenylphosphine catalyst system with excess triphenylphosphine was used this document gives no indication as regards the amount of excess triphenylphosphine used. It is further doubtful whether results obtained with a much longer olefin (octene) can be transferred to butene. Therefore (6) does not suggest the man skilled in the art that in a mixture of butenes, butene-1 is selectively hydroformylated yielding valeraldehyde with, according to an aspect of the existing problem, an n/iso ratio as indicated in Table 3 of the patent by applying the reaction conditions of the patent-in-suit.

5.3 The Appellants further argue that (3) (see page 2759, right column, middle) discloses that in a hydroformylation reaction with a Rh/triphenylphosphine catalyst excess of triphenylphosphine suppresses the rate of hydroformylation as well as the rates of the competing isomerisation and hydrogenation reactions. However, the last two are more strongly suppressed. The Appellants draw the conclusion that this teaching makes it obvious for the man skilled in the art that in a mixture of butenes, butene-1 will be selectively hydroformylated when excess phosphine ligand is applied. However, this part of (3) only deals with a relatively small excess of ligand (3 to 1 in Table 4 on page 2759) compared to the excess used in the patent-in-suit. If a man skilled in the art had nevertheless done as proposed he would not have achieved his aim, since this requires special reaction conditions, particularly as regards the ligand to Rh ratio defined above. Further a comparison of the relative rates of hydroformylation, hydrogenation and isomerisation gives no indication as to the selective hydroformylation of butene-1 in a mixture of butenes.

5.4 Document (3) (see page 2754, right column) further discloses that alk-1-enes react faster than alk-2-enes and iso-alkenes. However, a different catalytic system is used, since no excess of the triphenylphosphine is applied. Therefore, the statement that under these reaction conditions the alk-1-enes react faster than alk-2-enes and iso-alkenes would not have directed the man skilled in the art to the solution of the problem underlying the invention (see also paragraph 5.3).

5.5 Document (12) teaches that with a rhodium-hydride-carbonyl/phosphorus ligand catalyst olefins can be hydroformylated under relatively mild conditions (see column 1, lines 59-66). This document further teaches (see Example 3) that cis- and trans-butene as well as isobutylene can be hydroformylated using as catalyst tris(triphenyl-phosphine) rhodium-carbonyl-hydride/triphenylphosphine whereby the excess of triphenylphosphine is 35 mole per g-atom of Rh. Although this reaction is performed at higher hydrogen and carbon monoxide partial pressures (2100 kPa each) the skilled man will read this Example in context with the whole teaching of the document where it is said (column 1, line 59-66) that olefins can be hydroformulated under relatively mild conditions including temperatures from 0 to 250°C and pressures from 1 to 1000 at (10^2-10^5 kPa). Therefore the skilled man will expect from the teaching of (12) that the hydroformylation of a mixed C_4-olefin feedstock under mild conditions will result in the hydroformylation of all olefins present and thus yield a mixture of C_5-aldehydes. Document (12) thus points away from the invention.

Bearing this in mind the man skilled in the art would have expected that applying this process to a mixed C_4-olefin feedstock will only result in a mixture of aldehydes from which it is expensive to isolate n-valeraldehyde.

Therefore, he would have considered the reaction conditions as stated in the patent to be inappropriate for solving the problem and, with the economics of the process in mind, would have completely rejected the idea of hydroformylating a mixed C_4-feedstock to provide a suitable source of butene-1.

5.6 Therefore, in view of the problem underlying the claimed invention, the prior art cited did not give any indication that hydroformylation of a mixed C_4-olefin feedstock under the claimed reaction conditions will yield valeraldehyde with high n to iso ratio in an economic manner. Thus the process according to Claim 1 of the patent has to be considered as involving an inventive step.

5.7 The grounds for the patentability of the subject-matter of Claim 1 also apply to the subject-matter of independent Claim 9. Claim 9 merely claims a continuous process for the hydroformylation of a mixed C_4-feedstock essentially under the same reaction conditions as the batch process according to Claim 1.

Therefore the process according to Claim 9 has also to be considered as involving an inventive step.

5.8 Claims 2 to 8 and 10 concern particular embodiments of the process according to Claims 1 and 9 and thus are supported by the patentability of these claims.

Order

For these reasons, it is decided that:

The appeal is dismissed.

The Registrar: The Chairman:

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