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Aktenzeichen / Case Number / N° du recours : T 231/87 - 3.3.1

Anmeldenummer / Filing No / N° de la demande : 80 101 665.0

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Bezeichnung der Erfindung: Hydroformylation medium, process of production
Title of invention: thereof and process for producing aldehydes using
Titre de l'invention : the hydroformylation medium

Klassifikation / Classification / Classement : C07C 45/50

ENTSCHEIDUNG / DECISION

vom / of / du 1 December 1988

Anmelder / Applicant / Demandeur :

Patentinhaber / Proprietor of the patent /
Titulaire du brevet :

Union Carbide Corporation

Einsprechender / Opponent / Opposant :

BASF AG

Stichwort / Headword / Référence : Hydroformylation/Union Carbide

EPO / EPC / CBE Articles 54, 56, 84 and 100

Schlagwort / Keyword / Mot clé :

"Novelty (confirmed)" Inventive step
confirmed.
"Lack of clarity - not a ground for
opposition"

Leitsatz / Headnote / Sommaire

Europäisches
Patentamt

European Patent
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des brevets

Beschwerdekammern

Boards of Appeal

Chambres de recours

Case Number : T 231/87 - 3.3.1



DECISION
of the Technical Board of Appeal 3.3.1
of 1 December 1988

Appellant : BASF AG
(Opponent) D-6700 Ludwigshafen

Representative :

Respondent : Union Carbide Corporation
(Proprietor of the patent) Old Ridgebury Road
Danbury
Connecticut 06817 (US)

Representative : Barz, Peter Dr.
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Decision under appeal : Decision of the Opposition Division of the European
Patent Office of 4 November 1986, posted on
24 March 1987, rejecting the opposition filed
against European patent No. 0 017 183 pursuant to
Article 102(2) EPC.

Composition of the Board :

Chairman : K.J.A. Jahn
Members : R.W. Andrews
J.-C. Saisset

Summary of Facts and Submissions

I. The mention of the grant of the patent No. 0 017 183 in respect of European patent application No. 80 101 665.0, filed on 27 March 1980 and claiming priority from a prior application filed in the Federal Republic of Germany on 28 March 1979 and two prior applications filed in the United States of America on 16 July 1979 and 28 February 1980, was announced on 25 April 1984 (cf. Bulletin 84/17) on the basis of thirty-one claims. The independent Claim 1, 26 and 27 read as follows:

"1. A process for preparing a hydroformylation medium, said medium comprising a rhodium complex and triarylphosphine, which comprises mixing a rhodium complex concentrate with a sufficient amount of triarylphosphine so that there is at least 10 moles of free triarylphosphine per mole of rhodium present in said medium; said rhodium complex concentrate having been produced by a process which comprises concentrating a spent hydroformylation reaction medium that contains a partially deactivated rhodium complex catalyst, free triarylphosphine, aldehyde products and higher boiling aldehyde condensation by-products, into at least two separate material streams so as to remove free triarylphosphine, aldehyde products and higher boiling aldehyde condensation by-products from said spent hydroformylation reaction medium by means of distillation at temperatures of 20°C to 350°C and at pressures of 1.33 bar to 1.33×10^{-6} mbar (1000 to 1×10^{-6} mm Hg), wherein one stream is said rhodium complex concentrate distillation residue containing a major amount of the rhodium of said catalyst and which has been concentrated to 0.1 to 30 percent by weight

of said spent hydroformylation reaction medium, and the other material stream or streams consist essentially of one or more of the distilled volatile components of said spent hydroformylation reaction medium.

26. A hydroformylation medium comprising a rhodium complex and at least 10 moles of free triarylphosphine per mole of rhodium present in said medium, said rhodium complex having been derived from a rhodium complex concentrate which has been produced by a process which comprises concentrating a spent hydroformylation reaction medium that contains a partially deactivated rhodium complex catalyst and free triarylphosphine, into at least two separate material streams according to the process of any of Claims 1-25.
27. A hydroformylation process for producing aldehydes by hydroformylating an olefin with hydrogen and carbon monoxide in the presence of a hydroformylation medium comprising a soluble rhodium complex catalyst and at least 10 moles of free triarylphosphine per mole of catalytically active rhodium present in said medium, the improvement which comprises employing as a source of rhodium for said catalyst, a rhodium complex concentrate having been produced by the process of any of Claims 1-8, 12-19 and 21-26".

II. A notice of opposition was filed on 12 December 1984 requesting the revocation of the patent in its entirety in accordance with Article 100, paragraphs (a) and (b) EPC. The opposition was supported by the following documents:

- (1) US-A-4 148 830 and
- (2) Hydrocarbon Processing, pages 112 to 114, April 1970.

III. By a decision of 4 November 1986, posted on 24 March 1987, the Opposition Division rejected the opposition. The Opposition Division considered that the invention was disclosed in a manner sufficiently clear and complete for it to be carried out by the skilled person. The Opposition Division also found that the claimed subject-matter was novel and involved an inventive step in the light of the disclosure in the cited documents. In the Opposition Division's opinion the removal of free triarylphosphine by distillation from the spent hydroformylation medium served to distinguish the claimed subject-matter from the teaching of documents (1) and (2). With respect to inventive step the Opposition Division decided that the claimed process for the regeneration of a partially deactivated hydroformylation catalyst was not suggested by the disclosure of the cited prior art.

IV. An appeal was lodged against this decision on 21 May 1987 together with a statement of grounds for appeal and payment of the prescribed fee.

In this statement and at the oral proceedings held on 1 December 1988 the Appellant argued that the subject-matter of Claim 1 lacked novelty and did not involve an inventive step in the light of the disclosure in documents (1) and (2). He also alleged that Claim 1 did not fulfill the requirements of Article 84 EPC insofar as the claim lacked clarity. With respect to the latter objection the Appellant considered that the alleged lack of clarity arose from the fact that the extent to which the triarylphosphine was removed from the spent hydroformylation medium was not specified and the meaning of the expressions "spent hydroformylation medium" and "partially deactivated" and

the basis for the degree of concentration of 0.1 to 30% by weight were not clear. Thus, in the light of this lack of clarity in Claim 1, the Appellant considered that operating a hydroformylation process under quite normal conditions with the addition of triarylphosphine to replace any lost during the processing of the reaction mixture would fall within the scope of the present Claim 1.

With respect to novelty the Appellant submitted that a calculation, based on the data disclosed in document (2) and the assumption that the catalyst was present in the hydroformylation medium at a concentration of 1000 ppm of rhodium, revealed that the degree of concentration in this prior art process was about 7% by weight. Using the more realistic catalyst concentration of 500 ppm of rhodium resulted in a degree of concentration of about 3% by weight. The Appellant also alleged that during the usual working up of hydroformylation reaction mixtures by distillation as illustrated in, for example, document (2), it is inevitable that some triarylphosphine must be distilled off.

Furthermore, the Appellant argued that, since it is known in the art that the deactivation of the rhodium complex hydroformylation catalyst during use is caused by impurities in the feedstock and the formation of by-products, such as acroleins and alkyldiaryl- and dialkylarylphosphines, it is obvious that the removal of such impurities would result in an improvement in catalyst activity. Therefore, the removal of impurities which impair the activity of catalyst by distillation cannot be regarded as inventive. The addition of triarylphosphine to the concentrate thus obtained is a purely trivial measure.

- V. The Respondent replied that the teaching of Claim 1 of the patent in suit would be clear to the skilled person when read in the light of the general description and Examples. The claimed process was clearly novel and inventive in the light of the disclosure of document (1), since this document only taught the removal of the aldehyde product by distillation and Example 3 of the disputed patent demonstrates the unexpected effect achieved by the present process over this prior art process. Moreover, even if the skilled person were to repeat Example 11 of document (1) in the manner proposed by the Appellant the result obtained would not fall within the scope of the present Claim 1.

The Respondent also maintained that the claimed subject-matter was novel in the light of the disclosure in document (2) since the bottoms resulting from the distillation of the slip stream taken from the effluent from the aldehyde fractionator is not recycled to the hydroformylation reactor, but is further processed to effect a nearly quantitative recovery of the catalyst and triphenylphosphine by an undisclosed method. Moreover, the Appellant's calculation based on the teaching of this document could not destroy the novelty of the claimed process since it contained an assumption made by the Appellant. Furthermore, document (2) did not provide any information regarding the problem of catalyst regeneration in a hydroformylation process and the technical measure necessary to solve it.

With respect to the Board's doubts concerning the novelty of the subject-matter of Claims 26 to 31, the Respondent stated that the rhodium clusters resulting from the present process were distinguished by certain physical features from those in a spent hydroformylation medium and,

therefore, the subject-matter of these claims was patentable.

- VI. The Appellant requested that the decision be set aside and the patent in suit revoked. The Respondent requested that the appeal be dismissed.
- VII. At the conclusion of the oral proceeding, the decision was announced that the appeal is dismissed.

Reasons for the Decision

1. The appeal complies with Articles 106 to 108 and Rule 64 and is, therefore, admissible.
2. In view of the Appellant's objection that Claim 1 of the patent in suit does not comply with Article 84 EPC insofar as it lacks clarity, the Board finds it necessary to emphasise once again that the failure of the claims of an opposed European patent to fulfill the requirements of this Article does not constitute one of the grounds for opposition listed in Article 100 EPC.
 - 2.1 In the present case, the objection on the ground of lack of clarity was closely linked with an attack on the novelty of the subject-matter of Claim 1. However, if due to the unclear manner in which a claim has been drafted, a cited document may be held to anticipate the claim, a valid ground for opposition under Article 100(a) EPC is available to the Opponent.
3. The patent in suit relates to a hydroformylation medium, a process for its preparation and its use to produce aldehydes. The hydroformylation medium is prepared by

mixing a rhodium complex concentrate and a triarylphosphine wherein the said rhodium complex concentrate has been obtained as the distillation residue resulting from the concentration of a spent hydroformylation reaction medium to 0.1 to 30% by weight of said reaction medium under specified conditions of temperature and pressure. During this distillation free triarylphosphine, aldehyde products and higher boiling aldehyde condensation by-products are removed from the spent hydroformylation medium as distillate.

- 3.1 Before considering the question of the novelty of the claimed subject-matter it is expedient to indicate how the Board construes Claim 1 of the disputed patent.

In view of the fact that it is known that the catalytic activity of a rhodium complex decreases with use, the Board considers that the starting material for the claimed process is any hydroformylation medium which has been used to carry out a hydroformylation reaction and in which, therefore, the activity of the rhodium complex catalyst has fallen below its initial level. Furthermore, the expression "so as to remove free triarylphosphine" must be construed as meaning that the distillation of the spent hydroformylation medium is carried out in such a manner that a reasonable amount of triarylphosphine is contained in the distillate. This expression cannot be considered to include within its ambit the minute amounts of triarylphosphine possibly carried over during the distillation of the spent hydroformylation medium to separate the product aldehydes prior to its recycle to the hydroformylation reactor.

4. Document (1) discloses a process for the hydroformylation of α -olefins having 2 to 20 carbon atoms in the presence of

a rhodium complex catalyst and free triorganophosphine wherein higher boiling aldehyde condensation products containing hydroxyl groups are used as solvents (cf. Claim 1). In accordance with this prior art process the aldehyde products may be recovered from the hydroformylation reaction product mixture by passing the effluent from the hydroformylation zone after cooling and pressure reduction through a first long tube vaporiser to flash off hydrogen, carbon monoxide and unreacted α -olefin at ambient temperature and then through a second long tube to recover the aldehyde products as an overhead fraction. The liquid residue contains some unrecovered aldehyde products, free triorganophosphine, some high boiling condensation products and rhodium values (cf. column 10, lines 31 to 52). All or part of this liquid residue may be recycled to the hydroformylation zone (cf. Examples 13 and 14 and column 6, lines 16 to 20).

The operating conditions of the second long tube depends primarily on the nature of the aldehyde products and may be, for example, about 100°C or less to about 160°C or higher at 1.33 mbar to 1.013 bar (1 to 760 mm Hg) (cf. column 10, lines 44 to 49). Thus, this document does not disclose the removal of triarylphosphines by distillation from spent hydroformylation media. In the absence of such a teaching the claimed subject-matter is, therefore, novel.

- 4.1 The Appellant's arguments with respect to Example 11 of this document cannot alter the above finding since, even if one were to accept that, by combining Example 11 with the general teaching of this document, the skilled person would concentrate the spent hydroformylation media to approximately 25% by weight of the said medium by removing tridecanal, unreacted 1-octene and n-nonanal and α -methyloctanal, he would not take any steps to remove free

triphenylphosphine and would, therefore, not arrive at a result falling within the terms of Claim 1 of the disputed patent.

- 4.2 Document (2) describes a process for the preparation of aldehydes by hydroformylating olefins using a rhodium complex catalyst. After removal of carbon monoxide, hydrogen, unreacted olefin and saturated hydrocarbon from the reactor effluent it is fractionated to yield the aldehyde product overhead and a liquid residue consisting of solvent, catalyst and a steady-state concentrate of high boiling by-products. Most of this bottom product is recycled to the reactor, however, to prevent a build up of high boiling products, a small slip stream is removed. This slip stream is vacuum distilled to remove 70 to 80% of the high boiling products comprising the dimers and trimers produced by condensation of the aldehydes (cf. page 113, left-hand column, lines 3 to 22).

Thus, it is quite clear, in the absence of any positive steps to remove free triarylphosphine, the bottom product of this vacuum distillation column contains condensation by-products with boiling points higher than those of the above-mentioned dimers and trimers, free triarylphosphine and rhodium values. According to this document, this product is further processed to effect a nearly quantitative recovery of catalyst for recycle (cf. page 113, left-hand column, lines 22 to 24). In the right-hand column of page 113 at lines 19 to 25 of this document it is disclosed that make-up catalyst was obtained by processing part of the accumulated slip stream to recover 99.9% of the rhodium catalyst and excess triarylphosphine. In the absence of any disclosure relating to this procedure it must be assumed that it involved recovering the rhodium from the spent catalyst as rhodium metal and converting the

thus obtained rhodium metal into fresh catalyst. It was accepted by both parties at the oral proceedings that this assumption by the Board was correct.

Therefore, in the absence of any teaching in this document relating to the removal of free triarylphosphine from the spent hydroformylation medium by distillation, the subject-matter of Claim 1 of the patent in suit is also novel in the light of document (2).

- 4.3 The Appellant's assumption made in respect of catalyst concentration employed in the process according to document (2) renders any calculation using this assumption unsuitable as a basis for an attack on the novelty of the claimed subject-matter. However, even if one were to accept the figure for the catalyst concentration proposed by the Appellant, the result of this calculation would not destroy the novelty of Claim 1 since it shows that free triarylphosphine is not removed by distillation, viz 90g of triphenylphosphine in the initial reaction medium and 90g of triphenylphosphine remaining after the removal of all the volatile constituents from the spent hydroformylation medium.
- 4.4 Therefore, in the Board's judgement, the subject-matter of Claim 1 of the patent in suit is novel in the light of the teaching in both documents (1) and (2).
5. Claim 26, which relates to a hydroformylation medium when prepared by the claimed process, is also novel. At the oral proceedings, the Respondent convinced the Board that a fundamental change in the rhodium species present in the partially deactivated catalyst occurs during the claimed concentration process insofar as the resulting rhodium clusters are larger than those found in the partially

deactivated rhodium complex catalyst. The rhodium species obtained by the claimed process are also distinguished from those present in partially deactivated rhodium complex catalyst by the behaviour of the two species under hydroformylation conditions. Thus, with the former species the activity of the resulting catalyst initially increases with use up to a maximum value and then steadily decreases, whereas with the latter species the activity steadily declines.

- 5.1 In view of the above finding the subject-matter of Claim 27, which relates to the use of the rhodium complex concentrate when prepared by the claimed process, is also novel.
6. It is known that during use in the hydroformylation process the rhodium complex catalyst loses activity and eventually, after prolonged use, the activity of the catalyst will have decreased to such a point that it is no longer economically desirable to operate the hydroformylation process and the catalyst will have to be discharged and replaced by fresh catalyst. At the oral proceedings, it was agreed by both parties that before the priority date of the disputed patent the rhodium present in the deactivated catalyst was recovered as rhodium metal which could be then used to prepare fresh catalyst.

In the light of this prior art the technical problem underlying the patent in suit may be seen in providing a process for regenerating a partially deactivated rhodium complex catalyst in which the necessity of first recovering the rhodium in the partially deactivated catalyst as metal per se is avoided.

- 6.1 According to the disputed patent this technical problem is essentially solved by concentrating a hydroformylating medium containing the partially deactivated rhodium complex catalyst to 0.1 to 30% by weight of the said medium by distillation under specified conditions of temperature and pressure so as to remove free triarylphosphine, aldehyde products and higher boiling aldehyde condensation by-products as the distillate and leave a rhodium complex concentrate containing reactivated rhodium as the residue.

In the light of Examples 1, 2 and 4 to 23 of the disputed patent the Board is satisfied that this technical problem is plausibly solved.

- 6.2 Documents (1) and (2), which are not concerned with the problem of regenerating partially deactivated rhodium complex catalysts, do not provide the skilled person with any indication of how the above-defined technical problem may be solved.
- 6.3 It is known in the art that rhodium complex hydroformylation catalysts are deactivated by certain poisons which are normally present in the gases used as feedstock and that, even after the substantial complete removal of these poisons, catalyst deactivation still occurred. This deactivation was considered to be the result of certain by-products, such as substituted acroleins and alkyldiaryl- and dialkylarylphosphines, formed during the hydroformylation reaction. Thus, in his search for a solution to the above-defined technical problem, the skilled person might have considered removing such compounds by, for example, distillation from the spent hydroformylation reaction mixture. However, the skilled person was aware that high temperatures were considered to be detrimental to the rhodium complex catalyst and that the

presence of free triarylphosphine is essential for the success of the hydroformylation process. Even the knowledge that, during the distillation of the spent hydroformylation medium to remove the above-mentioned poisons, minute amounts of triarylphosphine could be present in the distillate, would not have provided him with any indication that the solution to the problem of reactivating the rhodium values of the spent hydroformylation catalyst lay in concentrating the spent hydroformylation medium to such an extent and under such conditions so as to remove free triarylphosphine which was considered to be an essential component of the catalyst.

Therefore, in the Board's judgement, the proposed solution to the technical problem underlying the patent in suit is inventive and the subject-matter of Claim 1 is patentable.

- 6.4 Claims 2 to 25, which relate to preferred embodiments of the process according to Claim 1, derive their patentability from this claim.
- 6.5 Claim 26 relates to a hydroformylation medium when prepared by the claimed process. This medium, which comprises a rhodium complex concentrate and triarylphosphine, is a precursor of the active hydroformylation catalyst. Its employment as catalytic precursor in a hydroformylation process results in an increased rate of reaction above that obtained when the partially deactivated catalyst from which it is prepared is used under the same conditions. In view of the above arguments this result must be regarded as unexpected. Therefore, the subject-matter of this claim involves an inventive step.
- 6.6 In view of the above, Claims 27 to 31, which relate to the use of the hydroformylating medium in accordance with

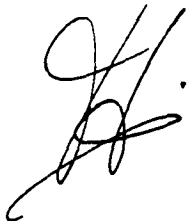
Claim 26 for the preparation of aldehydes, are also allowable.

Order

For these reasons, it is decided that:

The appeal is dismissed.

The Registrar:



The Chairman:

