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DECISION
of 21 January 1998

Case Number: T 0171/94 - 3.3.5

Application Number: 85201546.0

Publication Number: 0178008

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Language of the proceedings: EN

Title of invention:
Catalyst preparation

Patentee:
Shell Internationale Research Maatschappij B.V.

Opponent:
Exxon Research and Engineering Company

Headword:
Cobalt catalyst/SHELL

Relevant legal provisions:
EPC Art. 100(b), 56

Keyword:
"Sufficiency of disclosure (yes), inventive step (yes)"

Decisions cited:
-

Catchword:
-

Case Number: T 0171/94 - 3.3.5

DECISION
of the Technical Board of Appeal 3.3.5
of 21 January 1998

Appellant: (Proprietor of the patent)	SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V. Carel van Bylandtlaan 30 2596 HR Den Haag (NL)
Representative:	Aalbers, Onno P.O. Box 162 2501 AN Den Haag (NL)
Respondent: (Opponent)	Exxon Research and Engineering Company P.O. Box 390 Florham Park New Jersey 07932 (US)
Representative:	Somers, Harold Arnold ESSO Engineering (Europe) Ltd. Patents & Licences Mailpoint 72 Esso House Ermyn Way Leatherhead Surrey KT22 8XE (GB)
Decision under appeal:	**Decision of the Opposition Division of the European Patent Office posted 20 December 1993 revoking European patent No. 0 178 008 pursuant to Article 102(1) EPC.**

Composition of the Board:

Chairman: R. K. Spangenberg
Members: M. M. Eberhard
J. H. van Moer

Summary of Facts and Submissions

I. European Patent No. 0 178 008 based on application No. 85 201 546.0 was granted on the basis of ten claims.

II. The Respondent (Opponent) filed a notice of opposition requesting revocation of the patent on the grounds of lack of novelty, lack of an inventive step and insufficiency of disclosure (Article 100(a) and (b)). Of the documents cited by the parties during the opposition procedure, only the following remain relevant to the present decision:

D2: GB-A-2 104 405,
D12: Waatman and Prater, Ind. Eng. Chem., vol. 49, No. 2, 1957, pages 253 to 257,
D13: Neimark, Khelfez and Fenelonov, Ind. Eng. Chem. Prod. Res. Dev., vol. 20, 1981, pages 439 to 450,
D21: Weisz, Trans. Faraday Soc., vol. 63, 1967, pages 1801 to 1806,
D22: Same author and reference as D21, pages 1807 to 1814,
D23: Same author and reference as D21, pages 1815 to 1823,
D26: Respondent's experimental data in Appendix A of the letter dated 29 September 1993.

At the oral proceedings before the Opposition Division on 21 October 1993, the Appellant filed an amended claim 1, which reads as follows:

"1. A process for the preparation of catalysts comprising cobalt supported on a carrier, in which catalysts the cobalt is distributed over the carrier in such a manner as to satisfy the relation $\sum V_p/\sum V_c \leq 0.55$, wherein $\sum V_c$ represents the total volume of the catalyst particles under consideration and $\sum V_p$ is a value found by adding up the peel volumes present in the catalyst particles, the latter being regarded as being composed of a kernel surrounded by a peel, which kernel is of such a shape that at every point of the kernel perimeter the shortest distance (d) to the perimeter of the peel is the same, d being equal for all catalyst particles under consideration, and having been chosen such that the cobalt present in $\sum V_p$ is 90% of the quantity of cobalt present in $\sum V_c$, which process comprises immersing a porous carrier once or several times in a solution of a cobalt compound, removing the liquid from the composition followed by calcining after each immersion and activating the composition, such that during each immersion the following relation between the viscosity measured at 60°C (v in cS) and the temperature (T in °K) of the solution and the immersion time (t in s) is satisfied $(\log v) \times 10^4 / t \times T \geq 1$."

III. The Opposition Division revoked the patent on the ground of lack of an inventive step. The decision was based on amended claim 1 filed on 21 October 1993 and claims 2 to 10 as granted. The Opposition Division took the view that the requirement of sufficiency of disclosure was met and that the process of claim 1 was new. It was also held that in view of the Respondent's data in D26 a distinction could not be recognised between the catalysts of the closest prior art D2 and the catalysts prepared according to the process of claim 1.

Concerning the inventive step of claim 1, the Opposition Division pointed out that it was known from the prior art, in particular from D12 and D13, that the impregnation time and the temperature and viscosity of the solution were significant parameters for determining the impregnation depth. It considered that the relation $(\log v)\times 10^4/t\times T\geq 1$ (hereinafter $R\geq 1$) did not offer a reliable means for obtaining by a simple process the desired peel-type catalysts satisfying the relation $\sum V_p/\sum V_c \leq 0.55$ (hereinafter $Q \leq 0.55$), so that the said relation $R\geq 1$ did not solve any particular technical problem. Furthermore, the Appellant had not evidenced that the problem of providing catalysts having an improved selectivity for C_5+ hydrocarbons in the Fischer-Tropsch synthesis compared to the catalysts of D2 was in fact solved by the process of claim 1. In these circumstances, the process and the use defined in claims 1 and 8 lacked an inventive step.

IV. The Appellant lodged an appeal against this decision and filed comparative tests (hereinafter D38) with the statement of grounds of appeal.

Oral proceedings were held on 21 January 1998. At the hearing, the Appellant deleted claims 8 to 10 and submitted an amended claim 1 to replace the previous one, as main and sole request. Amended claim 1 differs from claim 1 of 21 October 1993 by the incorporation of the sentence "and which catalysts have an external surface area of from 5 to 70 cm^2/ml when present in the form of a fixed bed" after the words "90% of the quantity of cobalt present in $\sum V_c$".

V. Concerning sufficiency of disclosure and inventive step of the claimed process, the Appellant presented inter alia the following arguments:

The Respondent's catalyst preparation submitted with the letter of 14 October 1993 (Appendix A) demonstrated that the skilled person was able to prepare the claimed catalyst without undue burden. The patent taught that both the relations $Q\leq 0.55$ and $R\geq 1$ had to be satisfied. If with a given porous support the skilled person did not achieve a catalyst with the desired $Q \leq 0.55$

although the relation R≥1 was satisfied, he would simply have adjusted the time of immersion or the viscosity in order to decrease Q. These experiments would have taken at the most a few hours. The comparative tests D38 demonstrated the wide applicability of the invention to different classes of catalyst carriers. The particle size of the carrier was derivable from the surface area in the catalyst bed stated in the description. The Respondent's data in the letter of 1 November 1994 showed that the skilled person was also able to carry out the process of the patent in suit with a titania carrier.

Concerning inventive step, the Appellant argued that D38 showed that catalysts prepared by the claimed process exhibited a higher selectivity to C_5+ hydrocarbons than catalysts corresponding to those of D2, at equal space time yield and, thus, that the problem of improving the C_5+ selectivity had been solved by the claimed process. Furthermore, the catalyst of D2 had the drawbacks that its stability was very low when used in a fixed bed for the Fischer-Tropsch synthesis as shown by the significant decrease in the CO conversion in example 3. A second disadvantage was that high activity and selectivity were obtained only in the presence of Pt and/or Pd, ie very expensive metals. Moreover, the method of preparation of the catalysts was much more laborious than the claimed process. The viscosity and immersion time were indeed mentioned in text books and numerous theoretical models among other parameters involved in the impregnation methods of porous materials; however D13 contained only theoretical considerations and gave no practical suggestions as to how to prepare in a simpler way a peel-type, cobalt-containing catalyst having good performance in the Fischer-Tropsch synthesis.

VI. In response to the statement of grounds of appeal and during the oral proceedings, before submission of amended claim 1 and deletion of claims 8 to 10 by the Appellant, the Respondent had put forward inter alia the following arguments:

The Appellant's re-interpretation of claim 1 to require meeting the two independent relations R and Q was not supported by the patent application as filed, and introduced new matter violating Article 123.

The Respondent's catalyst preparation in Appendix A of the letter dated 14 October 1993 showed that adjusting the immersion conditions so as to satisfy the relation $R \geq 1$ did not inevitably lead to the desired $Q \leq 0.55$. There was inadequate guidance in the description for a skilled person to arrive at the desired Q ratio. Furthermore, critical parameters, such as particle size distribution and porosity of the carrier, were not given in the description so that the patent provided not more than an invitation to experiment to find those parameters which would satisfy the Q relationship, which was an unreasonable and onerous requirement for the skilled person. Therefore, the requirement of sufficiency of disclosure was not met.

The catalysts of D2 showed the highest activity for and selectivity to C_5+ hydrocarbons of any supported cobalt catalyst disclosed prior to 1985. The Appellant had not demonstrated any improvement regarding activity and selectivity over the catalysts of D2. The alleged comparative data in D38 were worthless because of the differences in the metal loading level of the catalysts. For the results of the tested catalysts to be comparative, both the cobalt loadings and the Q values should have been the same.

The Respondent's data in D26 showed that the process of D2 led to a cobalt concentration at the surface and within the particle. Therefore, Figure 5 of D2 was not an idealised version, and a supported cobalt catalyst for Fischer-Tropsch synthesis having a $Q \leq 0.55$ was not new. Once he knew that catalyst particles with a limited depth of catalytic metal penetration were useful for the Fischer-Tropsch synthesis, the skilled person could readily have determined from prior publications the methodology to achieve any desired depth of penetration for any set of variables. D21, D22 and D23 disclosed a general relationship for the fraction "f" of a catalyst particle occupied by a metal and an operational parameter for a specific impregnation system. By following the teaching of these documents, one could readily have manipulated all the variables affecting depth of metal penetration during impregnation. For a given carrier of a given size, following the teaching of D21-D23 resulted in a relationship involving time, temperature and viscosity for any given fraction "f".

Nevertheless, the Respondent indicated at the oral proceedings that he had no objection to maintenance of the patent on the basis of amended claim 1 filed at the oral proceedings and dependent claims 2 to 7 as granted.

VII. Both the Appellant and the Respondent requested that the decision under appeal be set aside and that the patent be maintained on the basis of claim 1 submitted during the oral proceedings, claims 2 to 7 as granted and a description to be adapted.

Reasons for the Decision

1. The appeal is admissible.

2. Although both parties have requested maintenance of the patent on the basis of amended claim 1 submitted at the oral proceedings and dependent claims 2 to 7 as granted, the Board can, in view of Article 114(1), only set aside the decision under appeal and allow the requests if it is satisfied that the requirements of Article 102(3) are met. In the present case, it is in the Board's judgment not immediately apparent that the amendments made in claim 1 during the oral proceedings remove all objections previously raised. The Board has therefore examined whether these objections prejudice the requested maintenance of the patent.

3. The amended claims meet the requirements of Article 123(2) and (3) EPC. Claim 1 is based on the combination of claim 1 as originally filed with features disclosed in the original application: see page 4, lines 18 to 20, and original claim 10 as regards the external surface area of 5-70 cm^2/ml, and page 6, lines 27 to 28, in connection with the calcination after each immersion. As the relations $R \geq 1$ and $Q \leq 0.55$ were both already stated in original claim 1 and in the original description, their mention in amended claim 1 cannot introduce new matter. Dependent claims 2 to 7 correspond to the original claims 2 to 7. These amendments clearly limit the scope of the granted claims.

4. As shown by the Respondent in Appendix A of the letter dated 14 October 1993 and admitted by the Appellant itself, satisfying the relation $R \geq 1$ does not inevitably lead to a catalyst having the desired Q ratio, ie

$Q \leq 0.55$. Therefore, the question has to be examined whether the skilled person would be able to carry out the process of the patent in suit without undue burden. For the preparation of the catalyst, the skilled person would start from a spherical porous silica particle having an external surface area of 5-70 cm^2/ml when in the form of a fixed bed, in particular 13 cm^2/ml, as stated in the patent in suit. The particle size of the silica sphere can be calculated from these data. Following the teaching of the patent, he would choose the viscosity, temperature and immersion time such that the relation $R \geq 1$ is satisfied, for example those indicated in table I for the catalysts where both the relations $R \geq 1$ and $Q \leq 0.55$ are satisfied. If the Q ratio of the catalyst thus obtained were greater than 0.55, then the skilled person would infer from the patent in suit that he could either decrease the immersion time or increase the viscosity to decrease Q while still satisfying the relation $R \geq 1$. It was not contested by the Respondent that such an adjustment of the immersion time or eventually the viscosity would need no more than two or three tests which would take at most a few hours, so that this adjustment does not put an undue burden on the skilled person. The particle size distribution of the silica carrier is not stated in the patent in suit. However, as argued by the Appellant, the skilled person is aware of the fact that catalysts with a broad particle size distribution cannot be used in the fixed bed of a commercial plant because of the pressure drop, and would therefore use a commercially available carrier having a narrow particle size distribution. Furthermore, the Appellant's comparative tests D38 show that the process of the patent in suit is also applicable to carriers having different shapes, particle sizes, surface areas, pore volumes and mean pore diameters. As regards the material of the carrier, silica, alumina and silica-alumina are indicated as suitable examples in the patent. The Respondent's preparation of catalyst B30 in Appendix II of the letter dated 1 November 1994, in which only one immersion was performed, shows that the skilled person was also able to perform the claimed process using titania extrudates. For the preceding reasons, the Board considers that the requirement of sufficiency of disclosure is met over the whole area defined in claim 1.

5. None of the cited documents discloses a process comprising the combination of features as defined in claim 1, in particular an immersion under such conditions that the relation $R \geq 1$ is satisfied. Therefore, the subject-matter of claim 1 is new.

6. Turning to the issue of inventive step, the Board considers in agreement with the parties and the Opposition Division that D2 represents the closest prior art.

This document discloses a method for producing a catalyst suitable for use in the Fischer-Tropsch synthesis, comprising cobalt and palladium or platinum or mixtures thereof supported on a porous carrier. This method comprises the step of immersing a support carrying Pd or Pt into a solution of cobalt carbonyl or a precursor thereof, in an appropriate solvent, and heating the mixture in a stream or under pressure of gaseous hydrogen and carbon monoxide or hydrogen for a period of time sufficient to form the catalyst. Heating is carried out at a partial pressure in the range from about 3 to 3000 psi and at a temperature between 100 and 350°C. The catalyst can be separated from the solvent and dried at temperatures preferably under 120°C (see page 3, lines 11 to 50; claims 1, 2, 4 and 6). The catalyst is said to have the idealised layered structure as depicted in Figure 5.

6.1 The Respondent's tests in D26, in which catalysts were prepared following the method disclosed in D2, confirm that the inhomogeneous cobalt distribution shown on Figure 5 is indeed obtained when performing the process under the operating conditions indicated in D2, and that this process leads to a catalyst having a quotient $Q \leq 0.55$. The SEM/EDS scan analyses in D26 show a cobalt concentration at the surface of the pellets but also some cobalt deposited within the pellet in a thin zone close to the periphery thereof. In this connection, it should be noted that the present claim 1 embraces the case where Q is very small and does not state whether or to which extent cobalt has penetrated into the carrier material. Although the catalyst preparation in D26 was carried out at a pressure lower than in example 4 of D2, all the operating conditions lie within the ranges indicated in D2. The Respondent's argument that the lower pressures would not have any significant effect on the nature of the final catalyst was not contested by the Appellant.

6.2 The catalysts of D2 can be used in the Fischer-Tropsch hydrocarbon synthesis in the slurry form or in the conventional fixed bed or fluidised bed (see page 3, lines 62-64). They are preferably used in the slurry form, and exhibit a superior activity as compared to conventional Fischer-Tropsch catalysts. They produce highly desirable products composed of a fraction of linear hydrocarbons ranging from C_1 to C_{40} with a low degree of branching. The catalysts lead for example to highly linear paraffinic products of an average chain length of 18 with little or no aromatics, unsaturates, oxygenates or branched products (see abstract; page 1, lines 32 to 49; page 4, lines 22 to 39; page 5, table 1; page 6, table 2; example 4). As indicated in the decision under appeal and not contested by the Appellant, the catalysts of D2 have a high selectivity for C_5+ hydrocarbons. As pointed out by the Appellant at the oral proceedings, the catalysts of D2 have the drawbacks that they exhibit high activity and selectivity only in the presence of platinum and palladium, ie very expensive metals, and that their method of preparation is relatively laborious.

6.3 Starting from D2, the technical problem underlying the claimed process can thus be seen in the provision of a less laborious method for the preparation of a supported cobalt catalyst having good performances in the Fischer-Tropsch hydrocarbon synthesis, in particular high C_5+ selectivity, even in the absence of platinum or palladium.

This problem is solved by the process as defined in claim 1, which requires in particular that both the relation $R \geq 1$ and the ratio $Q \leq 0.55$ be satisfied. This process differs from the method of D2 in that (i) the viscosity of the solution measured at 60°C, the temperature of the solution and the immersion time are chosen so as to satisfy the relation $R \geq 1$ during each immersion, (ii) the liquid is removed from the composition before calcining and (iii) the external surface area of the catalyst is from 5 to 70 cm^2/ml when present in the form of a fixed bed. It can be inferred from the data reported in Table II of the description that a supported cobalt catalyst which has a ratio $Q \leq 0.55$ and which has been prepared such that the relation $R \geq 1$ is satisfied during each immersion exhibits a high selectivity for C_5+ hydrocarbons even in the absence of platinum or palladium. Furthermore, it is plausible that the claimed process is less laborious than the process of D2 since it does not require the use or the formation of cobalt carbonyl, ie a toxic product, and involves a very simple impregnation method. Therefore, in the absence of evidence to the contrary it is credible that the said technical problem has been effectively solved.

6.4 D2 itself does not contain any information which could give the skilled person an incentive to perform the immersion under the conditions stated in claim 1 in order to solve the problem stated above.

In the decision under appeal, reference was made to the disclosure of D12 and D13. The latter deals with the theory of preparation of supported catalysts and discloses a theoretical analysis of the processes taking place during impregnation of porous supports, drying and thermal treatment. According to D13, the principles of distribution of an active component on the surface of the support pores depend on the type of binding between a "precipitated" component and the support surface and also on the mass-transfer conditions in the pores. On the basis of the adsorption isotherm, three types of catalysts are distinguished, ie catalysts of the sorption type, catalysts of the impregnated type and sorption-impregnated catalysts (page 440, left-hand column, fourth paragraph to page 441, second paragraph). In connection with the wet impregnation, D13 refers to the Weisz equation and to the sorption-diffusion mechanism studied by Weisz in D21 to D23 as well as to the generalised Weisz-Hariott theory which is said to describe satisfactorily the eggshell distribution in sorption catalysts (see page 441, left-hand column). D13 also discloses equations relating to the capillary impregnation (dry impregnation) and teaches that the latter ensures a more uniform macrodistribution of an active component than wet impregnation. Equation (7) indicated on page 442 illustrates the dependence of the time for filling a capillary on the viscosity of the solution, surface tension, capillary radius, and length of the capillary (see page 441, right-hand column, last paragraph, to page 442, left-hand column, second paragraph). Different regimes of drying and their influences on the distribution of the active component on the support surface are also studied in the case of an adsorbable component and a non-adsorbable component.

In the Board's judgment, therefore, D13 mainly discloses theoretical considerations in connection with the impregnation step and the drying step and mentions numerous parameters influencing the distribution of the active component in the pellet. In the passage concerning regulation of the distribution by introduction of competitive substances (page 441, right-hand column), information is given about the appropriate competitive agent leading to the eggshell distribution in the concrete case of impregnation of alumina with hexachloroplatinic acid. However, D13 is silent about the impregnation of a porous support with a cobalt compound and does not disclose which kind of interaction or mechanism is involved in this case. D13 also does not deal with the problem of producing a supported cobalt catalyst having good catalytic performances in the Fischer-Tropsch synthesis. In these circumstances, the theoretical teaching of D13 would have been of little assistance to the skilled person confronted with the practical problem of providing a less laborious method for the preparation of a supported cobalt catalyst having good catalytic performances in the Fischer-Tropsch synthesis, in particular high C_5+ selectivity, even in the absence of platinum or palladium. In the Board's judgement, the theoretical considerations in D13 would thus not have suggested choosing the viscosity and temperature of the solution and the immersion time so as to satisfy the relation $R \geq 1$ and the ratio $Q \leq 0.55$ in order to solve the problem stated above.

6.5 D12, which is referred to in D13, also mentions the equation giving the penetration time of a liquid into a cylindrical capillary (see equation (3) on page 254), ie the equation corresponding to equation (7) in D13 in the case of complete wetting. It is also pointed out in this document that adsorption plays a fundamental role in determining the distribution and amount of activating material found on the catalyst (see page 254, right-hand column). Adsorption properties of chloroplatinic acid, sodium chloride, aluminium nitrate and nickel nitrate on different porous supports are disclosed in D12; however this document does not contain any information concerning the preparation of supported cobalt catalysts nor does it deal with the problem of producing supported cobalt catalyst having a high C_5+ selectivity in the Fischer-Tropsch synthesis. Therefore, the skilled person could not have inferred from this document that the technical problem stated above would be solved by selecting the viscosity and temperature of the cobalt compound solution and the immersion time such that both the relation $R \geq 1$ and the ratio $Q \leq 0.55$ are satisfied.

6.6 D21, D22 and D23, which are referred to in D13 and were disregarded by the Opposition Division, disclose a general diffusion-sorption model based on the assumption of constant concentration in the external impregnation solution. In D23 this model is applied to the impregnation of spherical porous silica-alumina supports with dyes. These documents do not deal with the preparation of cobalt supported catalysts or with the technical problem stated above and contain no information which could hint at the claimed solution. The Weisz relationship disclosed in D21-D23 for the generalised time parameter T_u involves many parameters; however, neither the viscosity of the impregnation solution nor its temperature is mentioned in this relationship. The Board is not convinced that the skilled person would, without previous knowledge of the relation R≥1, have obviously derived the latter from the Weisz relationship. The fact that the results reported in the examples of the patent in suit might be in agreement with the theoretical curves predicted by Weisz does not prove that the teaching of D21-D23 would have suggested the claimed solution.

6.7 It follows from the above that the process according to claim 1 meets the requirement of inventive step set out in Articles 52(1) and 56 EPC.

7. Claim 1 being allowable, the same applies to dependent claims 2 to 7, whose patentability is supported by that of claim 1.

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 maintain the patent on the basis of claim 1 submitted at the oral proceedings, claims 2 to 7 as granted and a description to be adapted.

The Registrar: The Chairman:

A. Townend R. Spangenberg

H. Eb