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European Patent
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Boards of Appeal

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des brevets
Chambres de recours



Case Number : T 63 /85

DECISION of 10 March 1987 **correcting errors**
in the decision of the **Technical Board of Appeal 3.3.2**
of 9 December 1986

Appellant : The Dow Chemical Company
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Representative : Hann, Michael, Dr.
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Respondent : SOLVAY & Cie, S.A., Bruxelles
(Opponent) Département de la Propriété industrielle
Rue de Ransbeek, 310
B-1120 Bruxelles

Representative :

Composition of the Board :

Chairman : P. Lançon
Member : G. Szabo
Member : E. Persson

In view of computer transcription errors which inadvertently deleted from or repeated certain lines in the print-out of the Decision given on 9 December 1986, the text of the Decision is hereby corrected in accordance with Rule 89 EPC, as follows:

(i) page 5, insert at top:

"VII. The Appellant argued in the proceedings and at the oral hearing substantially as follows:",

(ii) page 7, delete from the bottom of the page the lines:

"involves the removal of the sulphate by the addition of barium chloride. The evidence showing a non-confidential correspondence from Solvay (2) is indicative of the fact that at least some commercial grades of hydrated calcium chloride have been known to have insoluble impurities and",

and,

(iii) page 9, insert at top:

"calcium, barium, and magnesium salts (2))but necessarily barium sulphate in a quantity more than 0.1% (cf. submitted letter (11)) than these known materials are identical with".

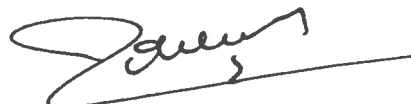
The Registrar:



00888



The Chairman:



Veröffentlichung im Amtsblatt	J/Nein
Publication in the Official Journal	Yes/No
Publication au Journal Officiel	Oui/Non

19

Aktenzeichen / Case Number / N° du recours : T 63/85

Anmeldenummer / Filing No / N° de la demande : 80 100 089.4

Veröffentlichungs-Nr. / Publication No / N° de la publication : 13 569

Bezeichnung der Erfindung: Hydrated calcium chloride reversible phase change
Title of invention: compositions with nucleating additives and method
Titre de l'invention : for their preparation

Klassifikation / Classification / Classement : C 09 K 5/06

ENTSCHEIDUNG / DECISION

vom / of / du 9 December 1986

Anmelder / Applicant / Demandeur :

Patentinhaber / Proprietor of the patent /
Titulaire du brevet :

The Dow Chemical Corporation (appellant)

Einsprechender / Opponent / Opposant :

Solvay & Cie (respondent)

Stichwort / Headword / Référence :

EPO / EPC / CBE Article 56 EPC

Kennwort / Keyword / Mot clé : "Inventive step - no one-way street situation"

Leitsatz / Headnote / Sommaire



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D E C I S I O N
of the Technical Board of Appeal 3.3.2
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B-1120 Bruxelles

Representative :

Decision under appeal : Decision of Opposition Division of the European Patent
Office dated 24 January 1985 revoking European patent
No. 13 569 pursuant to Article 102(1) EPC

Composition of the Board :

Chairman : P. Lançon
Member : G. Szabo
Member : E. Persson

Summary of Facts and Submissions

I. European patent No. 13 569 was granted on 23 June 1982 with three claims in response to the European patent application No. 80 100 089.4 filed on 9 January 1980 claiming the priority of the earlier application (US-2828) of 12 January 1979. Claims 1 to 3 were worded as follows:

1. A reversible liquid/solid phase change composition comprising hydrated CaCl_2 and a nucleating additive, characterized in that one or more of BaI_2 , BaSO_4 , or BaO are added to the composition in an amount effective to suppress supercooling of the hydrated CaCl_2 liquid phase.

2. A composition according to Claim 1 wherein the supercooling is 2°C or less.

3. A method of preparing a composition according to Claim 1 or 2 characterized by a uniform admixing of the ingredients.

II. The Opponent filed opposition against the European patent on 9 March 1983 requesting that it be revoked on grounds of lack of novelty and obviousness. The opposition was, *inter alia*, supported by:

(1) Schneider, M., et al, "Conception de chauffage solaire en domaine méditerranéen", Résumés des communications aux journées internationales d'étude sur le chauffage solaire dans le bâtiment. Liege, September 1977.

(2) Letter of Solvay & Cie, of 15 June 1976 and enclosed Bulletin of 8 July 1976

(3) VDI-Bericht No. 288, 1977

(4) DE-A-2 550 106.

In the course of opposition proceedings the claims were amended and directed to the use of calcium chloride hexahydrate to which 0.005 to 2.0 wt % sodium sulphate, iodide and/or oxide had been added as a reversible liquid-solid phase composition.

III. The Opposition Division revoked the patent in a decision of 8 November 1984 (oral hearing). The reason for the revocation was that (1) disclosed the use of hydrated calcium chloride from the Solvay process for heat storage and that such materials had somewhat suppressed supercooling properties. They contained sufficient amounts of barium sulphate among their insoluble impurities. Thus the claimed product was not novel. The step of adding excess barium sulphate to such material could not involve an inventive step, thus the amended use claim was also unpatentable.

As regards the other additives, since both barium chloride and fluoride were known nucleators for the purpose, there was a one-way street situation which led to the use of iodide. As regard the oxide, Hawley's "The Condensed Chemical Dictionary" (5) disclosed (page 154) that hydrated calcium chloride must lose $4H_2O$ above $30^\circ C$ and there would therefore be enough water available to convert the oxide to the hydroxide which was another known nucleator (4). None of the three barium salts in the claim was therefore associated with patentable subject-matter.

IV. The proprietor of the patent filed an appeal against the decision on 21 February 1985 with the payment of the fee and submitted a Statement of Grounds on 24 May 1985. The

Appellant filed new claims on 3 November 1986, together with auxiliary sets. Those were further amended at an oral hearing held on 9 December 1986. Claims 1, 3 and 4 of the main request are as follow:

- "1. A method of preparing a reversible liquid/solid phase change composition comprising hydrated CaCl_2 and a nucleating additive characterized by adding to hydrated CaCl_2 an amount of BaSO_4 of from 0.005 to 2.0 weight % to suppress supercooling of hydrated CaCl_2 liquid phase to 2°C or less and uniform admixing of the ingredients.
3. A reversible liquid/solid phase change composition comprising hydrated CaCl_2 and a nucleating additive, characterized in that, BaI_2 is added to the composition in an amount of from 0.005 to 2.0 weight % to suppress supercooling of hydrated CaCl_2 liquid to 2°C or less.
4. A reversible liquid/solid phase change composition comprising hydrated CaCl_2 and a nucleating additive, characterized in that, BaO is added to the composition in an amount of from 0.005 to 2.0 weight % to suppress supercooling of hydrated CaCl_2 liquid phase to 2°C or less."

Claim 1 of the first auxiliary request for relief is as follows:

- "1. Use of calcium chloride hexahydrate to which 0.005 to 2.0 weight percent BaSO_4 , BaI_2 and/or BaO has been added as a reversible liquid/solid phase change composition."

Claim 2 of the second auxiliary request is as follows
(Claim 1 being identical to Claim 1 of the third auxiliary request):

"2. A reversible liquid/solid phase change composition comprising hydrated CaCl_2 and a nucleating additive, characterized in that, BaO is added to the composition in an amount of from 0.005 to 2.0 weight % to suppress supercooling of hydrated CaCl_2 liquid phase to 2°C or less."

Claim 1 of the third auxiliary request is as follows:

"1. A reversible liquid/solid phase change composition comprising hydrated CaCl_2 and a nucleating additive, characterized in that, BaI_2 is added to the composition in an amount from 0.005 to 2.0 weight % to suppress supercooling of hydrated CaCl_2 liquid phase to 2°C or less."

VI. The following additional documents were also referred to by the parties:

- (6) JP-A-51-43387/1976
- (7) Licheri, G. J. Am. Chem. Soc., 1979,
- (8) Carlsson, Bo, et al, Solar Energy North, SEAS, International Conference 1978, and
- (9) Carlsson, Bo, et al, Storage of Low-Temperature Heat in Salt-Hydrate Melts, The Royal Institute of Technology, Stockholm, 1978
- (10) Winnaker, K., Technologie Minérale, 1962, page 391
- (11) Letter from Solvay of 22 January 1974
- (12) Chem. Abstr. 1976, 85, 145698 y (JP-B-76 70193) and
- (13) Chem. Abstr. 1978, 88, 138621 b.

VII. The Appellant argued in the proceedings and at the oral hearing substantially as follows:

(a) Ternary mixtures, containing substantial amounts of magnesium chloride, were disclosed in (1) and not binary mixtures according to the invention. The former had suppressed supercooling properties but this could rather be attributed to magnesium, in view of the statements in (6) and was deteriorating on repeated use.

(b) The evidence submitted by the Respondent, suggesting that certain hydrated calcium chloride materials had sufficient amounts of barium sulphate contamination was not convincing, since the document (2) in question and the further correspondence (11) related to special materials. In any case it was not known which particular contamination caused the suppression of supercooling, as the references were of general character (cf. (1) and (9)). Both (3) and (4) demonstrated that normal commercial material supercooled, contradicting the allegation of the Respondent that the Solvay material was already suitable for the purpose.

(c) Although the hydrate would certainly lose water above 30°C, this should only apply to open systems. Only in open vessels would some of the liberated water evaporate. Although the molten state contains tetrahydrate or dihydrate in solution (cf. phase diagram in (8), Fig. 4), a communication (7) indicated that the water is bonded in such circumstances as in the solid state. Experimental evidence showed that water was not available for converting barium oxide to hydroxide in such circumstances. X-ray spectra demonstrated no signals for the hydroxy compound. Thus success with the oxide could not have been anticipated by the use of the hydroxide, and was surprising and not obvious.

(d) As to barium iodide, there was no suggestion in the state of the art that this would be useful. The "chemical" approach to obviousness was wrong, since the physical characteristics were decisive when considering capability as a nucleator. Thus the chloride and fluoride suggested in no way the possibility of a useful effect with the iodide.

VIII. The Respondent submitted substantially the following arguments:

- (a) The use of commercial Solvay material was widespread everywhere. The process itself necessitated the removal of sulphate with barium chloride, hence the inevitable traces of the sulphate (10). The evidence made it clear that the main insoluble impurity was barium sulphate (cf. (2) and also (10)). The original claim covered the composition of document (1), and as far as the amended version was concerned, it was known from (1) that the alkali earth salts, notably barium sulphate, in the Solvay material suppressed supercooling, and their addition was therefore obvious.
- (b) The same should apply to barium oxide which was converted into the hydroxide. The X-ray tests were clearly insufficient to show that this was not taking place at the level of the additive. It was also known that other barium salts, including the chloride and fluoride (cf. (3), (12) and (13)), showed up as nucleators, and there was no good reason to doubt that the iodine salt would provide the same effect.

- IX. The Appellant requests that the decision under appeal be set aside and the patent be maintained on the basis of Claims 1 to 5 as submitted during the oral proceedings, or as auxiliary requests, on the basis of Claim 1, as filed on 3 November 1986, or Claims 1 to 3, (second auxiliary set) or Claims 1 and 2 (third auxiliary set), submitted during the oral proceedings, in that order of preference. The Respondent requested that the appeal be dismissed.

Reasons for the Decision

1. The appeal complies with Articles 106 to 108 and Rule 64 EPC and is, therefore, admissible.
2. The amendment of the claims in the main and auxiliary requests raises no objections on formal grounds since the limitations are supported by the disclosure in the specification (cf. in particular page 3, lines 9-12) and earlier Claims 2 and 3.
3. The patent relates to the suppression of supercooling compositions containing hydrated calcium chloride. Such compositions were already known from (1), (3) and (4), having various alkali metal salt contaminations, in particular barium, magnesium and strontium salts, as nucleators in order to prevent undesirable supercooling below the solidification point of hydrated salt. Citation (1) suggests that the calcium chloride component of the mixed hydrated calcium-magnesium chloride composition was of the Solvay type. It is common general knowledge that this type dominates the European market and its manufacture involves the removal of the sulphate by the addition of barium chloride. The evidence showing a non-confidential correspondence from Solvay (2) is indicative of the fact that at least some commercial grades of hydrated calcium chloride have been known to have insoluble impurities and

involves the removal of the sulphate by the addition of barium chloride. The evidence showing a non-confidential correspondence from Solvay (2) is indicative of the fact that at least some commercial grades of hydrated calcium chloride have been known to have insoluble impurities and within these, barium sulphate is present in significant amounts. The technical problem in respect of such publications was to provide alternative compositions with the same or further suppressed supercooling properties.

4. The three solutions of the technical problem presented in the patent are based on the addition of barium sulphate, oxide and iodide, respectively, as defined in various claims. Claim 1 of the main request relates to the sulphate being added in an amount from 0.005 to 2 % weight % to achieve a suppressed supercooling of 2°C or less. This can, according to Sample 3 of the Example, be achieved, although the result requires 170 test cycles before the effect is reliably attained. The feature specifying a maximum of 2°C supercooling is only meaningful if the other features of the definition would not in themselves guarantee such result in all instances. This functional requirement indicates that the claim not only envisages the use of the purest materials but also others where the supercooling may be also influenced by other impurities leaving, however, room for improvement by the addition of barium sulphate within the specified range.
5. It appears from (1) that Solvay type of hydrated calcium chloride was already incorporated in heat storage compositions, and that this particular component, like the other components used, contained certain impurities, including alkali earth salts, which were capable of suppressing supercooling. If, as the evidence shows, at least some grades of Solvay calcium chlorides not only contained characteristically alkali earth salts (i.e.

calcium, barium, and magnesium salts (2)) but necessarily barium sulphate in a quantity more than 0.1% (cf. submitted letter (11)) then these known materials are identical with the product obtained by the method of Claim 1 and any novelty of its subject-matter lies entirely in the "addition" of that component rather than the incidental presence owing to its origin and manufacture.

6. The closest prior art for the method claim is therefore the preparation of such commercially available grade which happens to contain substantially more barium sulphate than the minimum of 0.005% required for the purpose. The upper limit of 2% in the amended claim is, in any case, irrelevant and not limiting since "no further benefit is achieved after about 2%" according to the specification (page 3, line 10). The only remaining problem, i.e. in alternative manufacture of the same known grade of calcium chloride, is solved according to the patent now by purposefully adding the required amount of barium sulphate to a starting material containing less than what is required in this respect and uniformly admixing the ingredients. There can be no inventive step in providing the known material by admixing its known ingredients in the usual manner since the attainment of the same product in this manner represents no unexpected effect, even if someone discovers a new use for such known product (except in cases of therapeutic or diagnostic use according to Article 54(5) EPC). The claim requires no other precaution or condition, and even allows the presence of other impurities (cf. above in 4). Thus the subject-matter of Claim 1 of the main request is obvious. The same applies to Claim 2 which merely specifies a hexahydrate type of composition, well known in the state of the art. Some of the rest of the claims will be hereinafter assessed in connection with the auxiliary requests.

7. The first auxiliary request comprises a claim which covers, *inter alia*, the use of the product obtained according to the method claimed in the main request, as discussed above. Whilst the claim is also novel, in as much as it incorporates the same novel step of deliberately adding barium sulphate to the hexahydrate of calcium chloride, the application of such material, as a reversible composition, cannot be accepted as inventive either. Any Solvay material was already recommended for such purposes in admixture with magnesium chloride (1), and it was emphasized that it contained itself, like the other components, alkali earth metal salts which reduced supercooling. Any barium sulphate content was expected to contribute to such beneficial effect, whether carried forward from manufacture or specifically added, like the other members of the same salt group.
8. The skilled person aware of the problem of providing such an effect, had knowledge of the documents (cf. also (3), (4), (12) and (13), which recommended the chloride, fluoride, hydroxide and carbonate for the purpose. It appears that the well-known virtual insolubility of the sulphate was not discouraging when the salt was intended to be used as a nucleator. The usual capability was therefore expected, and the supercooling effect, up to 5°C (cf. Table II of the specification) gave no clear indication of reliable improvement. If anything, the alleged absence of diminishing effect with other salts is offset by a very long period of initial less satisfactory performance with barium sulphate. In view of the fact that this time the claim is not limited to the maximum of 2°C or less supercooling, implies that a worse effect is envisaged. Thus, the effects disclosed in the Example, including the range from 3 to 5°C, is no better than that mentioned in (3), which suggests this in relation to barium carbonate and fluoride.

9. The argument that no reliable physical theory predicts the behaviour of such salts, cannot be followed. Predictions are not only based on deductions from theory but could also rely on inductive inferences on grounds of empirical observations. In fact four specifically mentioned salts of barium, as well as a number of strontium and magnesium salts, were known to act as nucleators which was very suggestive of a good chance for an effect in the right direction for any choice in the alkali earth metal salt area. The results with barium sulphate are no better than what was envisaged. Obviousness may not only be at hand when the improvements are expected, but also when their absence is foreseen (cf. "Gelation/EXXON", T 119/82, OJ 5/1984, 217, 227 and Headnote II). Thus the first auxiliary request cannot be granted either.

10. The closest prior art for the barium oxide variant of Claim 2 of the second auxiliary request is (4) which describes the use of barium hydroxide as a nucleator, reducing the supercooling to 4.2°C. The use of barium oxide provides similar results since supercooling was maximised in the Example to 3°C. Whilst the subject-matter of the claim is apparently novel when the composition is formed in view of the distinction between oxide and hydroxide, it was suggested by the Respondent that the small amount of oxide would necessarily be transformed into the hydroxide and then function as such, as described in the above citations.

11. The loss of water by the hexahydrate above 30°C is not only suggested by (5) but is also demonstrated by the phase diagram in (8), Fig. 4. If the hexahydrate was fully turned into a one-phase melt above 32°C (cf. the diagram for 51% calcium chloride), and at least some of it was available for evaporation according to the admission of the

Appellant, this must be indicative of some differences in bondages when compared to the solid state. The communication (7) merely suggested that some of the relative arrangements were "similar", but no explanation was given as to which of the three molecules of water nearer to the cation and the six further away was retained in this manner.

12. The X-ray spectra submitted at the oral hearing, without any written explanations assisting reproductibility, allegedly showed that absolutely no hydroxide was formed from the 10% barium oxide added to the system. No information was offered, in spite of questioning, as to the limits of sensitivity of the test system. The absence of conspicuous peaks characteristic of the hydroxide may simply mean that these signals were below the considerable noise level in the tests. Since the signals were admittedly roughly proportional to the quantities involved, there was no way to estimate their expected strength for instance at the relevant level of 0.005% in the system.
13. The Respondent submitted evidence in the form of the cited documents, which was sufficiently indicative of the strong *prima facie* possibly of transitions from oxide to hydroxide. The Appellant failed on his part to refute the presumption, since this was a question of very small amounts of material and not of substantial masses. Apart from the strong possibility that the oxide is only a precursor for the agent in the known method using hydroxide, it was also clear to the Board, that in any case the change to yet another alternative barium compound did not bring any significant improvement and the composition was therefore performing only as expected for many alkali earth metal salts in general and cited barium salts in

particular. The variety in question lacks inventive step and therefore independent Claim 2 falls and with it the second auxiliary request, although Claim 1 could have been accepted as it can be seen hereunder.

14. The third request only relates to the incorporation of barium iodide. The closest state of the art is (3) suggesting a performance of 3-5°C supercooling for the fluoride analogue. Whilst the same kind of effect was not unexpected for the iodide either, the technical problem for this particular variant was to improve the performance significantly. The solution of this particular problem, as defined in Claim 1 truly suppresses supercooling to 2°C or less. Sample 2 of the Example demonstrates that no supercooling at all was observed for 20 cycles which appears to be significantly better than that attained by the most relevant prior art (3), there being no quantitative data about the performance of barium chloride in (13). Such improvement was therefore unexpected since otherwise the suppression only achieves the 3 to 5°C level irrespective of the choice of the alkali earth metal salt. There being no expectation of improvement, the skilled person had no good reason to explore the possibility with this particular variant in preference of other possible choices. No one-way-street situation can therefore be recognised leading inevitably to a "bonus effect" (cf. Moulding compositions/BAYER", T 192/82, OJ 9/1984, 415, 425 and Headnote II). The claimed subject-matter is therefore not obvious and the same applies to the dependent Claim 2.

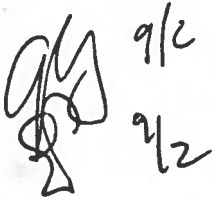
Order**For these reasons,****it is decided that:**

1. The decision of the Opposition Division is set aside.
2. The case is remitted to the Opposition Division with the order to maintain the patent amended with claims according to the third auxiliary request as submitted in the oral proceedings and with an appropriately adapted description.

The Registrar:



The Chairman:



9/12
9/12