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**D E C I S I O N**  
**of 23 April 1997**

**Case Number:** T 0652/93 - 3.3.2

**Application Number:** 89309574.5

**Publication Number:** 0366258

**IPC:** B01J 39/20

**Language of the proceedings:** EN

**Title of invention:**

Process for preparing cation exchange resins having improved stability and cation exchange resins prepared therefrom

**Patentee:**

THE DOW CHEMICAL COMPANY

**Opponent:**

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**Headword:**

Cation Exchange Resing/DOW

**Relevant legal provisions:**

EPC Art. 56

**Keyword:**

"Inventive step (yes, after amendment)"

**Decisions cited:**

T 0002/83

**Catchword:**

-



Case Number: T 0652/93 - 3.3.2

**D E C I S I O N**  
of the Technical Board of Appeal 3.3.2  
of 23 April 1997

**Appellant:**

THE DOW CHEMICAL COMPANY  
2030 Dow Center  
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**Representative:**

Allard, Susan Joyce  
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**Decision under appeal:**

Decision of the Examining Division of the  
European Patent Office posted 19 March 1993  
refusing European patent application  
No. 89 309 574.5 pursuant to Article 97(1) EPC.

**Composition of the Board:**

**Chairman:** R. K. Spangenberg  
**Members:** M. M. Eberhard  
J. Van Moer

## Summary of Facts and Submissions

- I. European patent application No. 89 309 574.5 was refused by a decision of the examining division announced orally on 5 February 1993, with written reasoning posted on 19 March 1993. The decision was based on an amended set of nine claims, namely claim 1, filed on 6 January 1993, and claims 2 to 9, filed on 25 November 1991 (claims 2 to 7 (in part) were resubmitted unamended on 6 January 1993).
- II. The ground for the refusal was that the subject-matter of these claims did not involve an inventive step over the disclosure of the citations US-A-3 342 755 and CS-A-235 485 (hereinafter D2 and D1 respectively).

The examining division held that the problem of stabilising the copolymer matrix of an ion-exchange resin in order to make it less susceptible to oxidation degradation was known from D2. A skilled person faced with this problem would have applied the teaching of D1 (ie the use of an antioxidant additive) to the present case because the real problem was not specifically to protect either the functional groups or the polymer matrix but in fact to scavenge free radicals and avoid the chemisorption of oxygen, and consequently to prevent the degradation of the ion-exchange resin. The examining division took the view that the selection of particular antioxidants, such as those defined in claims 2 to 6, was within the competence of a skilled person endeavouring to look for antioxidants other than those of D1.

III. The appellants lodged an appeal against this decision. They filed a set of amended claims 1 to 6, as the main request, on 26 June 1993, together with the statement of grounds of appeal, and referred to new documents in support of their arguments. Comparative tests were submitted on 7 March 1996 and on 24 March 1997. Claim 1 of the said request reads as follows:

"1. The use of a substituted monohydroxy benzene antioxidant in preparing a stabilized cation exchange resin comprising a copolymer matrix of a monovinyl aromatic monomer and a divinyl aromatic monomer which is functionalized with sulfonic acid groups, in order to reduce the amount of copolymer matrix decomposition products released during use, the substituted monohydroxy benzene being incorporated into the cation exchange resin in an amount of at least 0.001 percent by weight based on the weight of the cation exchange resin."

IV. In a communication from the board, the appellants' attention was drawn to a document illustrating the common general knowledge about the use of antioxidants in polymers, namely "Encyclopedia of Polymer Science and Engineering", vol. 2, 1985, pages 73-91 (hereinafter D7).

Oral proceedings were held on 23 April 1997. At the hearing, the citation mentioned by the appellants both on page 2 of the application and in their letter of 6 January 1993, namely "Prediction and Identification of Leachables from Cation Exchange Resins", Proceedings of the 48<sup>th</sup> International Water Conference, 2-4 November 1987 (hereinafter D4), was also taken into consideration.

- V. The appellants put forward **inter alia** the following arguments:

It was well documented in the literature and organic chemistry textbooks that carbon-functional group degradation of aromatic sulfonates, such as cation exchange polymers, occurred by an electrophilic substitution mechanism which did not involve "free radicals" or "chemisorption of air oxygen" as suggested in D1. Accordingly, a skilled person reading D1 would have dismissed its teaching as being incorrect or irrelevant with regard to cation exchange resins containing sulfonate groups and would not have expected antioxidants, which were generally effective against free radical processes, to affect the loss of functional groups at all. Furthermore, there was no teaching in D1 to suggest the stabilisation of a cation exchange resin containing sulfonate groups with a monohydroxybenzene, nor did D1 disclose the use of any monohydroxybenzene as an antioxidant.

A skilled person would also not have combined the teaching of D2 and D7 since the latter document was concerned with polymers without functional groups on the benzene ring. The skilled person could not have expected that the mechanism of oxidation of polymers by a free-radical chain reaction and the effect of hindered phenol antioxidants both described in D7 might apply likewise to sulfonated ion-exchange resins. Although the decomposition products of the cation exchange resins were identified in D4, this document did not teach that the degradation mechanism involved a free-radical mechanism. On the contrary, since Figure 2 of D4 showed a relatively small amount of

phenolsulfonic acid in the decomposition products of the sulfonated cation exchange resin, this document rather suggested that the oxidation was based on a mechanism different from that involved in the oxidation of unsulfonated polystyrene polymers.

- VI. The appellants requested that the decision under appeal be set aside and that a patent be granted on the basis of claims 1 to 6 filed on 26 June 1993 and a description to be adapted.

### **Reasons for the Decision**

1. The appeal is admissible.
2. The amended claims 1 to 6 are considered to meet the requirements of Article 123(2) EPC. Claim 1 is based on the combination of features disclosed in claims 1, 3, 7 and 8 as originally filed and in the original description. In particular, it is stated at page 4, lines 23 to 26 thereof that the copolymer matrix is functionalised with sulfonic acid groups. Furthermore, it is directly and unambiguously derivable from the original description that the antioxidant is incorporated into the cation exchange resin to improve the stability thereof, in particular to reduce the amount of copolymer matrix decomposition products released during use: see page 3, lines 27-31; page 4, line 29 to page 5, line 6; page 11, lines 26-31; page 13, lines 24-31 and page 14, lines 28-30. Therefore, the use of the antioxidant in a process for preparing a stabilised cation exchange resin in order to achieve the reduction in the amount of decomposition products released during use as defined in claim 1 finds support in the application as filed. The features of the dependent claims 2, 3 and 4 are disclosed in the

original description at page 6, lines 25-27, lines 28-31 and lines 32-34 respectively. The features recited in claims 5 and 6 are disclosed in the original claims 9 and 7.

3. None of the documents cited in the course of the examining or appeal procedure discloses the use of a substituted monohydroxy benzene antioxidant in the process for preparing a stabilised cation exchange resin comprising a copolymer matrix of a monovinyl aromatic monomer and a divinyl aromatic monomer, the copolymer matrix being functionalised with sulfonic acid groups. Therefore the use as defined in claim 1 is new over the cited documents.
  
4. D2, which relates to the improvement of the oxidation stability of sulfonated crosslinked polystyrene cation exchange resins during their use, is considered to represent the closest prior art.

This document discloses that sulfonated crosslinked polystyrene cation exchange resins, in particular those resins comprising a sulfonated styrene/divinyl benzene copolymer, fail to withstand the degrading effects of oxygen, chlorine and other oxidising agents usually found in feed waters. According to D2, one of the explanations given for the degradation of polystyrene resins by an oxidising agent is that a weak link exists in the polymer at the tertiary carbon adjacent to the benzene ring of the styrene moiety of the polymer. The weakness of the link is believed to be primarily due to the tendency of oxygen or oxidising agents to form hydroperoxides with the hydrogen on the tertiary carbon. The hydroperoxides subsequently split the carbon chain to form lower molecular weight degradation products, accompanied by a gradual reduction in the degree of crosslinking in the resin. D2 teaches that the oxidation resistance of these cation exchange

resins, in particular their stability against the degradative effects of oxidising agents present in feed waters in the process of softening and demineralising aqueous solutions, can be improved by halogenating the crosslinked styrene/divinyl benzene copolymer before sulfonation (see column 1, lines 31-48; column 2, lines 12-29; claims 1 and 2). According to the present application, this process has in particular the drawback that large amounts of halogenating agents are required for achieving significant improvements of the oxidation resistance (see page 3, first complete paragraph).

Starting from this prior art, the technical problem underlying the present application can be seen in providing a method for improving the stability of cation exchange resins during use, in particular for improving their ability to withstand decomposition primarily caused by oxidation, which method does not have the said drawback.

According to amended claim 1 of the present application, this problem is solved by using a substituted monohydroxy benzene antioxidant in the preparation of the sulfonated copolymer matrix, this antioxidant being incorporated into the copolymer matrix in an amount of at least 0.001 wt.%. In view of the examples of the present application, which show a significant reduction in the amounts of decomposition products released from the cation exchange resin during its use, and taking into account that no halogenating agent is involved for the stabilisation of the ion exchange resin, the board is satisfied that the said problem has actually been solved by the use as defined in claim 1.



- 4.1 D2 itself does not contain any information suggesting an alternative route for improving the stability of cation exchange resins not involving the use of large amounts of halogenating agents.
- 4.2 D7 discloses the use of antioxidants to protect polymers against degradation caused by reaction with atmospheric oxygen. It is explained that the mechanism by which a polymer undergoes autoxidation involves a free-radical chain reaction and that hydrogen-donating antioxidants, such as hindered phenols and secondary aromatic amines, inhibit oxidation by competing with the polymeric substrate for peroxy radicals. A hindered monophenol, such as 2,6-di-tert-butyl-4-methylphenol, is mentioned on page 86 as an effective antioxidant for protecting polystyrenes against degradation by oxidation. Hindered phenols are said to protect thermoplastic polymers during processing and in use, the concentrations usually ranging from 0.01 to 0.5%, depending upon the polymer and the severity of use conditions (see all of page 73; page 75, paragraphs titled "Radical Scavengers" and "Hindered Phenols"; page 78, lines 1 to 3; page 86, table 4, the first compound of the monophenols). The question arises whether in view of D7, a skilled person would have contemplated applying this teaching to cation exchange resins of the kind described in D2, ie sulfonated styrene/divinyl benzene copolymers, in order to solve the problem stated above. In this context, the appellants submitted that the mechanism of oxidative degradation of the sulfonated cation exchange resins was not known before the priority date and that a skilled person could not have expected the said mechanism to be similar to that described in D7 for the degradation of polymers because of the presence of the sulfonate group on the aromatic rings in the cation exchange resins.

4.3 The main decomposition products released by cation exchange resins after long-term use have been identified in D4 as being 4-phenolsulfonic acid, 4-sulfobenzoic acid, sulfonated oligomers and polymers of sulfonated polystyrene (see page 73, summary). Although this document discloses that these main decomposition products are the result of the oxidative attack of the copolymer backbone of the cation exchange resin (see page 70), no further information is provided about the decomposition mechanism of these cation exchange resins. At the oral proceedings, the appellants pointed out that it could be inferred from Figure 2 of D4 that the amount of 4-phenolsulfonic acid was relatively small, ie less than 10% of the decomposition products released by the cation exchange resin. Taking into account that the oxidation of cumene by a free-radical mechanism results in important amounts of acetone and phenol, the skilled person would have expected a greater amount of 4-phenolsulfonic acid to be present in the decomposition products released by the sulfonated cation exchange resins if their oxidative degradation had involved an analogous free-radical mechanism of reaction. However, as emphasised by the appellants, the amount of 4-phenolsulfonic acid in the decomposition products is very small according to D4. In these circumstances, the board can accept the appellants' arguments that even in view of the teaching of D2 and D4, it was still not clear to the skilled person before the priority date which mechanism of reaction was involved in the long-term oxidative degradation of cation exchange resins based on a sulfonated styrene/divinyl benzene copolymer. In the absence of clear information in this respect in the prior art, a skilled person would not have been prompted in view of D7 to incorporate a substituted monohydroxy benzene antioxidant into the sulfonated cation exchange resins since he could not have reasonably expected, in view of the degradation

products reported in D4, that this incorporation might lead to a sufficient improvement of the oxidation resistance of the said cation exchange resins during use as in the case of polystyrene polymers (see T 2/83, OJ EPO 1984, 265).

- 4.4 D1 deals with the problem of degradation of anion and cation exchange resins during grinding and further processing for the production of heterogeneous ion-exchange membranes. On page 3 of D1, it is disclosed that the prolonged grinding of the ion-exchange resin causes local overheating of the particles and mechanico-chemical stress on the polymer structure. This results in the appearance of free radicals, chemisorption of oxygen and consequent degradation processes which cause the deterioration, above all, of the active surface of the ion-exchanger particles. Such particles have poor electrical conductance, the anion exchange resins having in particular a low chemical stability under these conditions because of their labile quaternary ammonium groups (see page 3, second and third paragraphs). According to D1 these shortcomings are avoided by grinding the ion-exchange resin in the presence of a water-soluble ionic antioxidant additive, the active ionic part of which is capable of binding to the ion-exchange resin. Salts of hydroxylamine, guanidine or hydrazine are used to protect the cation exchange resins from degradation during grinding (see all of page 4; page 5, lines 1 to 4; claims 1 and 2).

As pointed out by the appellants, the problem of long-term stability of cation exchange resins during their use is not addressed in this document. Furthermore, D1 does not disclose the use of a substituted monohydroxy benzene antioxidant for protecting cation exchange resins against oxidative degradation during use. Hydroxyquinone, ie a

dihydroxybenzene, is mentioned on page 5 but only for the protection of anion exchange resins. D1 does disclose the appearance of free radicals during grinding, but also mentions local overheating and mechanico-chemical stress as well as poor electrical conductance of the resulting particles without indicating which part of this disclosure concerns the cation exchange resins or the anion exchange resins. The mechanism by which sulfonated cation exchange resins oxidise and degrade during use cannot be inferred from this document. Therefore, even in view of D1, a skilled person would not have been encouraged to apply the teaching of D7 to sulfonated styrene-divinylbenzene cation exchange resins as disclosed in D2 or D1 in order to solve the problem of stability during use stated above.

- 4.5 The remaining documents cited during the examining procedure and published before the priority date are less relevant than the preceding ones and cannot, therefore, hint at the claimed solution either.
- 4.6 It follows from the above that the use as defined in amended claim 1 meets the requirement of inventive step set out in Articles 52(1) and 56 EPC.
5. Claim 1 being allowable, the same applies to dependent claims 2 to 6 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 grant a patent on the basis of claims 1 to 6 filed with the letter of 23 June 1993 and a description to be adapted.

The Registrar:

The Chairman:

P. Martorana

R. Spangenberg

