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Bezeichnung der Erfindung / Title of invention / Titre de l'invention : A process for hydrogenation of carbon-carbon double bonds in an unsaturated polymer

Klassifikation / Classification / Classement : C08C 19/02

ENTSCHEIDUNG / DECISION

vom / of / du 14 March 1989

Anmelder / Applicant / Demandeur : The Goodyear Tire and Rubber Company

Patentinhaber / Proprietor of the patent / Titulaire du brevet :

Einsprechender / Opponent / Opposant :

Stichwort / Headword / Référence : Hydrogenation/Goodyear

EPÜ / EPC / CBE Article 56

Schlagwort / Keyword / Mot clé : "Inventive step (confirmed) - identification of closest prior art"

Leitsatz / Headnote / Sommaire

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Case Number : T 33/87 - 3.3.1

DECISION
of the Technical Board of Appeal 3.3.1
of 14 March 1989

Appellant : The Goodyear Tire & Rubber Company
1144 East Market Street
Akron, Ohio 44316 (US)

Representative : Weyland J.J.P.
Goodyear International Tire Technical Center
Patent Department
Avenue Gordon Smith
L-7750 Colmar-Berg (LU)

Decision under appeal : Decision of Examining Division 010 of the European Patent Office dated 18 September 1986 refusing European patent application No. 84 630 023.4 pursuant to Article 97(1) EPC

Composition of the Board :

Chairman : K.J.A. Jahn
Members : R.W. Andrews
C.V. Payraudeau

Summary of Facts and Submissions

I. European patent application No. 84 630 023.4 (publication No. 0 117 221), filed on 17 February 1984 claiming priority of 22 February 1983 from a prior application filed in the United States of America, was refused by a decision of the Examining Division 010 of the European Patent Office dated 18 September 1986. The decision was based on Claims 1 to 10 as originally filed.

II. The stated ground for the refusal was that the claimed subject-matter did not involve an inventive step. The Examining Division considered that the proposed solution to the problem of providing a process capable of hydrogenating carbon-carbon double bonds in the main or side chains of an unsaturated polymer in the latex form was obvious in the light of the disclosure in US-A-4 221 872 (1), Encyclopedia of Chemical Technology, Kirk-Othmer, 3rd Edition, Volume 12, page 743, 1980 (2) and Organic Syntheses Collections, Volume 5, pages 281 to 285, 1973 (3).

Although documents (2) and (3) did not disclose the hydrogenation of carbon-carbon double bonds in polymers, the Examining Division considered that these documents proved that the hydrogenation of carbon-carbon double bonds by hydrazine in the presence of an oxidising agent and, optionally, cupric ions was a standard method in organic chemistry. Since it was known from document (1) that the carbon-carbon double bonds of pendant allyl groups of ion exchange resins may be hydrogenated using diimine, it was prima facie obvious to apply the same method to unsaturated polymers in the latex form in the absence of any teaching which would deter the skilled person from investigating the feasibility of this method.

III. An appeal was lodged against this decision on 26 November 1986 together with the prescribed fee. With the statement of grounds of appeal filed on 5 December 1986 the Appellant submitted an amended statement of claim, amended pages 1 to 4 of the description and an affidavit reporting the results of several experiments showing that the process described in document (1) could not be used to hydrogenate carbon to carbon double bonds of a polymer in latex form.

The Appellant contended that the process disclosed in document (1) is used to remove the residual unsaturation present in pendant allyl groups of macroporous ion exchange resins and that it is carried out in a reaction medium which is a solvent for hydrazine and also capable of swelling the resin. Furthermore, there is no suggestion in this document or documents (2) and (3) that this prior art process would be applicable to polymers containing 5 to 100% by weight of conjugated diene monomers which are vastly different from the resins disclosed in document (1). The Appellant argued that, in view of the complex nature of latices, it must be considered surprising that an elastomeric polymer in the latex form can be hydrogenated by the claimed process without destroying the delicate balance of properties that are present in the latex.

IV. In a reply dated 8 April 1988 to a communication of the Board in which the opinion was expressed that the closest prior art in the light of which the technical problem underlying the application in suit should be determined would appear to be the article in Die Makromolekulare Chemie, Volume 163, pages 13 to 36, 1973 (4), referred to on page 2, lines 10 to 17 of the application, the Appellant argued that it would not be possible without the benefit of hindsight for the skilled person to select certain features from the various pieces of prior art and conclude that the hydrogenation of the double bonds in the backbone of a polymer in latex form would occur without detrimental impact on the physical properties of the latex.

With his reply filed on 20 December 1988 to a further communication from the Board in which formal objections were raised against the statement of claim filed with the above-mentioned letter, the Appellant submitted an amended statement of claim and amended pages 1 and 3 of the description.

V. The Appellant requests that the decision under appeal be set aside and a patent granted on the basis of the five claims filed on 20 December 1988. The only independent claim now reads as follows:

"A process for hydrogenating carbon-carbon double bonds of an unsaturated polymer prepared from 5 to 100 percent by weight of a conjugated diene monomer unit and 95 to 0 percent by weight of ethylenically unsaturated monomer units characterised by (a) combining the unsaturated polymer in latex form with (1) an oxidant selected from the group consisting of oxygen, air and hydroperoxides; (2) a reducing agent selected from hydrazine and hydrates thereof; and (3) a metal ion activator; (b) heating the mixture to a temperature of from 0°C to the reflux temperature of the reaction mixture."

Reasons for the Decision

1. The appeal is admissible.

2. There are no formal objections to the present Claims 1 to 5 since they correspond to Claims 1 to 5 as originally filed apart from an alteration to the dependencies of Claims 3 and 5.

3. The application in suit relates to a process for hydrogenating carbon-carbon double bonds of an unsaturated polymer prepared from 5 to 100% by weight of a conjugated diene monomer unit and 95 to 0% by weight of ethylenically unsaturated monomer units. Suitable unsatuated polymers are, for example, polyisoprene, polybutadiene, styrene/butadiene copolymers, acrylonitrile/butadiene copolymers, butadiene/isopropene copolymers, isoprene/isobutylene copolymers and natural rubber. The removal of unsaturation results in polymeric materials which have greater resistance to oxidative and thermal degradation.

3.1 From the decision under appeal it is clear that the Examining Division considered that document (1) represented the closest prior art. This document discloses a process for the preparation of an ion exchange resin by hydrogenating an ion exchange resin comprising unquaternised amino groups and unsaturated olefinic bonds with diimine in a reaction mixture (cf. Claim 1). The diimine being generated <u>in</u> <u>situ</u> by known methods such as reaction of hydrazine with an oxidising agent or from precursors such as azodicarboxylates or arylsulphonohydrazides (cf. column 3, lines 34 to 62). From the disclosure of this document relating to suitable resins for hydrogenation by this prior art method (cf. column 4, line 20 to column 5, line 13 and Examples 1 to 4, 6 and 7), it is clear that these resins are very different from the elastomeric polymers in the form of latices used as starting materials for the presently claimed process.

3.2 In view of the differences in the substrates to be hydrogenated the Board has grave doubts as to whether document (1) represents the closest prior art, particularly in the light of the disclosure of document (4). This document discloses the hydrogenation of unsaturated polymers such as, for example, <u>cis</u>- and <u>trans</u>-1,4-polybutadiene, styrene/butadiene random copolymers, <u>cis</u>-1,4-polyisoprene, poly-2,3-dimethyl-1,3-butadiene and poly-2,5-dimethyl-2,4-hexadiene (cf. Table 1 on page 19) with diimine (diimide). Since these polymers fall within the definition of the unsaturated polymers in the present Claim 1 the Board takes the view that document (4) represents the closest prior art in the light of which the technical problem underlying the application should be determined.

3.3 This known hydrogenation is carried out by dissolving the unsaturated polymer in an aromatic solvent and generating the diimine <u>in</u> <u>situ</u> by thermally decomposing p-toluensulphonohydrazide at temperatures between 110°C and 160°C (cf. summary on page 13 and paragraph 3 on page 18). However, a disadvantage of this prior art process was considered to lie in the fact that it could not be used to hydrogenate an unsaturated polymer in latex form.

Therefore, in the light of this closest prior art the technical problem underlying the application in suit may be seen in providing a process for hydrogenating this type of unsaturated polymers in latex form.

3.4 According to the application this problem is essentially solved by reacting the unsaturated polymer in latex form with oxygen, air or a hydroperoxide, hydrazine or a hydrate thereof and a metal ion activator. In the light of the Examples, the Board is satisfied that this technical problem is plausibly solved.

4. After examination of the cited prior art the Board is satisfied that this technical teaching is not disclosed and

the claimed subject-matter is, therefore, novel. Since novelty is not disputed it is not necessary to consider this matter in detail.

5. It still remains to be examined whether the requirement of inventive step is met by the claimed subject-matter.

5.1 As previously mentioned, document (4) describes the use of diimine as a reagent for the homogeneous hydrogenation of unsaturated polymers. For application of this known hydrogenation reagent to unsaturated polymeric substrates p-toluensulphonohydrazide was selected as a suitable diimine-producing reagent from those potentially available since, of all the known reagents, p-toluenesulphonohydrazide would allow mutual solubility of the initial polymers, the product polymers and the hydrogenation agent at all degrees of conversion if the hydrogenation is carried out in an aromatic medium. This feature of common solubility was considered to be important for the successful implementation of the reaction (cf. first paragraph on page 23).

Thus, although this document teaches that the transitory species diimine may be used to hydrogenate carbon-carbon double bonds in unsaturated polymers of similar structure to those referred to in the present Claim 1, there is no teaching in this document which would provide the skilled person with the incentive to consider using other means of generating diimine or any indication of how the problem underlying the application of hydrogenation unsaturated polymers in the latex form may be solved.

5.2 Document (1) discloses the use of diimine to hydrogenate unsaturated olefinic bonds in macroporous ion exchange resins which are, as previously pointed out, very different in structure from the elastomeric polymeric substrates of the present process. In this prior art process it was essential that the reaction medium comprise a solvent in which hydrazine is soluble and, preferably, the solvent should also be capable of swelling the ion exchange resin so that good penetration of diimine will occur (cf. column 4, lines 5 to 8). Furthermore, a carboxylic acid function is preferably present, either in the ion exchange resin itself or an aliphatic or aromatic carboxylic acid may be added to the reaction medium (cf. column 3, line 65 to column 4, line 3). In contrast to the teaching of document (4) in which one method for generating the diimine is specified, according to this document any prior art method may be used in this process (cf. column 3, lines 34 to 62).

This document is completely silent on the possibility of applying the process disclosed therein to other polymeric substrates and contains no teaching which would suggest to the skilled person that this known process would be suitable for hydrogenating the carbon to carbon double bonds in elastomeric polymers prepared from 5 to 100% by weight of conjugated diene monomers in latex form. However, if the skilled person were to consider using this process by following the teachings of Examples 1 to 3 and 5 to 7 of this document to hydrogenate an elastomeric latex, such as a NBR latex containing 29% solids, he would find that the rubber immediately coagulated and no hydrogenation occurred (cf. Affidavit filed on 5 December 1986).

5.3 Document (2) discloses that olefins, acetylenes and azo-compounds are reduced by diimine (diazene) which may be generated from the reaction between hydrazine and oxidising agents, such as, oxygen, hydrogen peroxide, iodine, iodate, ferricyanide and the cupric ion, the acidification of the dipotassium salt of diazenedicarboxylic acid, or by heating p-toluenesulphonohydrazide in glycol. However, in the absence of any suggestion of the reduction of polymers or the use of a metal ion activator, this document provides no indication that the solution to the above-defined technical problem lay in generating the diimine in the manner specified in the present Claim 1.

5.4 Document (3) describes the reduction of <u>cis</u>, <u>trans</u>, <u>trans</u>-1,5,9-cyclododecatriene to <u>cis</u>-cyclododecene using aqueous 95% hydrazine, 95% ethanol, air and copper (II) sulphate pentahydrate. Thus, although this document discloses the use of a metal ion activator, it teaches that the use of ethanol is an essential constituent of the reaction medium. However, the skilled person is aware that the presence of ethanol in the reaction medium would destroy the delicate balance of properties found in a latex if this prior art method were to be applied in the hydrogenation of elastomeric latices. Moreover, in the Board's judgement this document would merely convey to the skilled person that the method disclosed therein is a convenient and general method for the selective hydrogenation of <u>trans</u> double bonds of medium sized ring systems. The skilled person would not be induced by the restricted teaching of this document to consider applying the method disclosed therein, with or without modification, in order to solve the present technical problem.

5.5 In considering the cited prior art it must be borne in mind that the reaction media in which those prior art processes were carried out comprised relatively few components, for example, polymer, solvent and p-toluenesulphonohydrazide (document (4)), ion exchange resin, hydrazine hydrate, sodium ions and acetic acid and optionally methanol (document (1)) and dodecatriene, hydrazine, ethanol and copper II sulphate pentahydrate (document (3)). Moreover, none of these components would adversely affect the hydrogenation reaction. However, the skilled person faced with the present technical problem is aware that a latex is an aqueous dispersion of polymeric substance stabilised by the presence of soaps and emulsifiers. Therefore, the skilled person, having studied the cited prior art, would not be in a position to conclude with any certainty that the hydrogenation of the carbon to carbon double bonds of a polymer in the latex form would occur without detrimental impact on the physical properties of the latex.

6. Therefore, in the Board's judgement, the subject-matter of the present Claim 1 involves an inventive step. Claims 2 to 5, which represent preferred embodiments of the process claimed in Claim 1, derive their patentability from this claim.

Order

For these reasons, it is decided that:

1. The decision under appeal is set aside.

2. The case is remitted to the Examining Division with the order to grant a patent on the basis of Claims 1 to 5 and pages 1 and 3 filed on 20 December 1988, pages 2 and 4 filed on 5 December 1986 and pages 5 to 17 as originally filed.

The Registrar: The Chairman: