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Bezeichnung der Erfindung: Compositions for forming epoxy adhesive containing acrylate rubber.
Title of invention:
Titre de l'invention :

Klassifikation / Classification / Classement : C 08 F 283/10

ENTSCHEIDUNG / DECISION

vom / of / du 19 May 1987

Anmelder / Applicant / Demandeur : Stauffer Chemical Company

Patentinhaber / Proprietor of the patent /
Titulaire du brevet :

Einsprechender / Opponent / Opposant :

Stichwort / Headword / Référence :

EPÜ / EPC / CBE Article 54(1)

Kennwort / Keyword / Mot clé : "Novelty"

Leitsatz / Headnote / Sommaire

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Case Number : T 247/86

D E C I S I O N
of the Technical Board of Appeal 3.3.1
of 19 May 1987

Appellant : Stauffer Chemical Company
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Decision under appeal : Decision of Examining Division 011 of the European Patent Office dated 27 March 1987 refusing European patent application No. 82 110 037.7 pursuant to Article 97(1) EPC

Composition of the Board :

Chairman : K. Jahn
Member : C. Gérardin
Member : G. Paterson

Summary of Facts and Submissions

I. European patent application No. 82 110 037.7, filed on 29 October 1982, claiming the US priority of an earlier application filed on 30 October 1981 and published under number 78 527 was refused by a decision of the Examining Division dated 27 March 1986.

II. The decision was based on the ground that the subject-matter of Claim 1 and independent Claim 9 was not novel with regard to the teaching of FR-A-2 343 009 (1).

The application contained 19 claims, of which Claims 1 and 9 read as follows:

Claim 1: "A reaction mixture, for forming a curable epoxy resin composition containing polyacrylate rubber, which comprises a major amount of epoxy resin, a minor amount of a monoethylenically unsaturated monomer capable of forming a polyacrylate rubber, and an effective amount of a monomer soluble initiator for forming the rubber from the monomer."

Claim 9: "An epoxy resin composition comprising a major amount of an epoxy resin and a minor amount of a polyacrylate rubber."

III. In the decision it was stated that document (1) describes the preparation of polyepoxides grafted by a mixture of ethylenically unsaturated acids (or anhydrides) and acrylates of aliphatic alcohols having 1 to 18 carbon atoms in the presence of an initiator which may be monomer soluble. Although the grafting reaction occurs rather quickly, there must be an intermediate period wherein a reaction mixture exists which contains a major amount of

epoxy resin, a minor amount of monoethylenically unsaturated monomer capable of forming a polyacrylate rubber and a monomer soluble initiator. This disclosure was considered to be novelty destroying for the subject-matter of Claim 1.

It was also stated that, since the preparation of a grafted polymer entails the production of small amounts of the homopolymer of the grafting monomer, the final reaction must comprise a polyacrylate rubber and an epoxy resin, whatever the exact structure - possibly grafted - of the latter. This teaching was considered to anticipate the subject-matter of Claim 9.

IV. On 2 May 1986 the Applicant filed a notice of appeal. The prescribed fee for appeal was paid on 26 May 1986. A statement of Grounds of Appeal was filed on 4 July 1986.

V. In a communication the Board indicated that not only document (1) would appear novelty destroying for the subject-matter of Claim 1, but FR-A-2 208 936 (document (2)) as well, wherein the polymerization of unsaturated monomers in presence of a cross-linking agent and a larger amount of epoxy resin is described.

Besides, the Appellant's attention was drawn to a further document, FR-A-1 275 954 (document (3)) whose subject-matter corresponds to specific embodiments envisaged in the application (example 5, Claim 8), such as the copolymerization of glycidyl (meth)acrylate and another acrylate or methacrylate in presence of an epoxy resin.

VI. The arguments presented by the Appellant in the Appeal stage including oral proceedings held on 19 May 1987 can be summarized as follows:

i) In the process disclosed in document (1) the acrylate monomer does not polymerize independently from the epoxy resin, but is grafted onto the latter. By contrast, in the mixture presently claimed no solvent is used; this means that the monomer concentration is such that polymerization occurs without grafting reactions, i.e. that the polyacrylate rubber is formed as a true rubber phase in admixture with a non-grafted epoxy resin. This is safeguarded by the feature of Claim 1 which defines the amount of monoethylenically unsaturated monomer as the amount capable of forming a polyacrylate rubber.

ii) Even if some polyacrylate rubber may be formed in the process described in document (1), the skilled man would not equate these undesired traces with the minor amounts as specified in Claim 9; moreover this polyacrylate rubber would then be admixed with an acrylate grafted epoxy resin, not with a true epoxy resin.

iii) Whether one considers the embodiment according to Claim 8 or Claim 9 of document (2), one always has a combination of epoxy resin, curing agent, monomer, cross-linking agent and initiator which has no similarity at all with the curable compositions specified in Claims 9 to 17 of the application.

iv) Document (3) teaches a copolymerization of glycidyl ester in an epoxy resin which acts as an inert solvent for the reaction whereas in the application the same glycidyl ester is described as a grafting agent for the rubber in the epoxy resin. In the prior art one has thus a dissolution, in the application, however, a true rubber phase.

VII. During oral proceedings held on 19 May 1987 the Appellant filed a new set of claims with a more restrictive definition of the grafting agent limited to compounds having a vinyl group and a carboxy group; after minor editorial amendments the claims read as follows:

1. A mixture for forming a curable epoxy resin composition containing polyacrylate rubber which consists of an epoxy resin in an amount of 65% to 99% by weight of the mixture, an amount of 49% to 1% by weight of the epoxy resin of an alkyl acrylate or alkyl methacrylate monomer or mixture thereof capable of forming a polyacrylate rubber having a Tg of less than 40°C, and an effective amount of a monomer soluble initiator for forming the rubber from the monomer, wherein the initiator comprises from about 0.01% to about 10% by weight of the monomer.

2. A mixture as claimed in Claim 1 wherein the epoxy resin comprises from 80% to 95% by weight of the composition and the monomer comprises from 25% to 5% by weight of the epoxy resin.

3. A mixture as claimed in Claim 1 which also contains a cross-linking agent for the rubber-forming monomer.

4. A mixture as claimed in Claim 1 which also contains, in addition, a grafting agent containing a vinyl group and a carboxy group for the polyacrylate rubber and epoxy resin, the grafting agent being present at from 0.1 to 20% by weight of the monomers forming the polyacrylate rubber.

5. An epoxy resin composition consisting of an epoxy resin in an amount of from 65% to 99% by weight of the composition and a polyacrylate rubber consisting of a polymer selected from the group consisting of the polymers of alkyl acrylates and/or alkyl methacrylates having a Tg of less than 40°C in an amount of from 49% to 1% by weight of the epoxy resin.

6. A composition as claimed in Claim 5 wherein, in addition, the rubber is cross-linked with a polyethylenically unsaturated cross-linking agent.

7. A composition as claimed in Claim 5 wherein the polyacrylate rubber and epoxy resin are grafted to one another with a grafting agent containing a vinyl group and a carboxy group.

8. A composition as claimed in Claim 5 wherein the epoxy resin is a glycidyl polyether of the reaction product between a polyhydric phenol and an epihalohydrin.

9. A composition as claimed in Claim 5 wherein the epoxy resin is present at 80% to 95% by weight of the composition and the rubber is present at from 25% to 5% by weight of the epoxy resin.

10. A curable adhesive system containing any of the epoxy resin compositions of Claims 5 to 9 and an effective amount for curing of an epoxy curing agent.

11. A curable adhesive system containing any of the epoxy resin compositions of Claims 5 to 9 and an effective amount for curing of an epoxy curing agent selected from the group consisting of polyamine, polyamine adduct and polyamide curing agents.

The set of claims submitted during the oral proceedings was partially in manuscript and was numbered 1 to 12, but it was agreed during such oral proceedings that Claim 5 was inconsistent with Claim 4 and should therefore be deleted. The intended deletion of Claim 5 is marked on the submitted set of claims. The claims set out above have, therefore, been renumbered 1 to 11 as a consequence of the deletion of Claim 5.

VIII. The Appellant requested that the decision under appeal be set aside and that a patent be granted on the basis of the claims submitted during oral proceedings.

Reasons for the Decision

1. The appeal complies with Articles 106 to 108 and Rule 64 EPC and is therefore admissible.

2. There are no formal objections on the basis of Article 123(2) EPC to the current version of the claims since it does not extend beyond the content of the application as filed.

In Claim 1 the amounts of the three components result from the incorporation of the ranges disclosed in original Claims 2 to 4. The features that the polyacrylate rubber has a glass transition temperature less than 40°C and that it is derived from alkyl acrylate and/or methacrylate monomer(s) are to be found on page 4, lines 23 to 28 of the description and Claim 15. The amendment of "comprises" into "consists of" provides a more limitative definition of the mixture and therefore is not objectionable.

Claim 4 corresponds to original Claim 7 to which the amount of grafting agent disclosed on page 6, lines 9 to 12 has been added and wherein the functional groups of the grafting agent mentioned on page 6, lines 1 to 3 have been specified.

Claim 5 corresponds to original Claim 9 and has been amended in a similar way as Claim 1 as far as the quantitative features are concerned and by incorporation of the definition of the polymer specified in original Claim 15. Claim 7 corresponds to original Claim 14 with the specification that the grafting agent contains a vinyl group and a carboxy group as originally disclosed on page 6, lines 1 to 3.

The other claims only differ by their number and the claim(s) they are related to.

3. The scope of the claims having been limited the objections which led to the rejection cannot be maintained as evidenced by a comparison between the prior art teachings and the subject matter of the three categories of claims.

4. The novelty of the subject-matter of Claims 1 to 4 drafted as reactive mixture claims will be discussed first.

4.1 The copolymerization described in document (1) requires the presence of a solvent (Claim 1; page 2, lines 23 to 29; page 6, lines 13 to 20; examples). By contrast the drafting of Claim 1 of the application which now specifies that the mixture consists of an epoxy resin, an acrylate/methacrylate monomer and an initiator, excludes the presence of any other compound. In particular, the presence of a solvent is excluded.

4.2 In the process disclosed in document (2) the initial mixture already contains a curing agent for the epoxy resin (Claim 1; page 2, lines 15 to 18), either in admixture with the resin (example 1 and Claim 8) or in admixture with a monomer (example 2 and Claim 9). This curing agent is not within the scope of Claims 1 to 4.

4.3 Document (3) relates to the copolymerization of 5 to 95 parts of an unsaturated glycidyl ester (Claim A1; page 2, column 2, lines 7 to 9 and formula) with 90 to 50 parts of an acrylate or methacrylate comonomer (page 3, column 1, lines 19 to 31; example 1) in the presence of an inert epoxy resin (page 1, column 2, lines 32 to 35; page 2, column 1, lines 7 to 13 and column 2, lines 3 to 9). This teaching, because of the additional presence of the unsaturated glycidyl ester in the monomer mixture, is clearly distinguishable from Claims 1 to 3; it is not relevant to Claim 4 either, because the grafting agents specified therein do not have a glycidyl group as reactive group.

4.4 The subject-matter of Claims 1 to 4 is thus novel with regard to the teaching of documents (1) to (3).

5. Likewise the novelty of the subject-matter of Claims 5 to 9 which are concerned with the compositions resulting from the reaction of the mixtures defined in Claims 1 to 4, will be discussed by reference to the same documents.

5.1 The reaction products described in document (1) contain the solvent used to carry out the grafting reaction; depending on the further use of the composition, this solvent may be eliminated from the graft polymer solution (page 6, lines 30 to 34; page 7, lines 29 to 31).

When the solvent is not eliminated, the composition is a ternary mixture of an epoxy resin, a polyacrylate rubber and a solvent which does not fall within the scope of Claims 5 to 9.

When the solvent is eliminated, novelty can be acknowledged for the subject matter of Claims 5 and 6 because of the additional use in the prior art of 2 to 10% by weight of an unsaturated carboxylic acid in the monomer mixture. However, the resulting polymer would fulfil the functional requirements specified in Claim 7. It is thus necessary to compare the actual polymers obtained in the presence of solvent (prior art) with those obtained in absence of solvent (present application), i.e. to examine which features of the polymer are affected by the presence of a solvent in the initial mixture.

5.1.1 As mentioned in Encyclopedia of Polymer Science and Technology, Volume 2, (1965), page 489, graft copolymerization may be effected by any of the conventional techniques of bulk, suspension, or emulsion polymerization, and in some cases by solution polymerization. However, in the latter case, the monomer concentration should be greater than the concentration of solvent diluent to achieve reasonably high grafting yields (paragraph 4). Although there is no specific teaching as to appropriate amounts of solvent to be used to carry out the grafting reaction in document (1), in practice large amounts are present. According to the examples the starting compositions contain 900 g of solvent (840 g with the epoxy resin and 60 g with the peroxide), 450 g of epoxy resin and 450 g of monomers wherefrom 30 g or 36 g of acrylic acid. This means that the solvent concentration is much higher than the grafting monomer concentration and that a low grafting yield is to be expected; the acid index indicated in the examples actually shows that the

grafting rate is lower than 30%. By contrast the decrease in acid number indicated in example 2 of the application (page 12, table) shows a substantial reaction rate of the carboxy groups with the epoxy groups (up to 96%).

5.1.2 Likewise solution polymerization, to which document (1) exclusively refers, leads to polymers with generally lower molecular weights than other processes, as stated in "Grundriss der makromolekularen Chemie", Volume 1, page 178, E. Vollmert, published in 1980 (third paragraph, last sentence). By contrast, in the absence of solvent or in concentrated solutions high molecular weights are obtained, especially in the case of methyl methacrylate, methyl acrylate and acrylic acid, as specified in "Textbook of Polymer Science", second edition, (1962, 1971), page 291, Wiley-Interscience (third paragraph).

5.1.3 There is thus no doubt that the grafting yield as well as the molecular weight of the polymers according to document (1) are significantly lower than in the present application; these two differences thus confer novelty on the subject-matter of Claims 7 to 9 as well.

5.2 For the reasons already given above, the teachings of documents (2) and (3) do not affect the patentability of Claims 5 to 9, because of the compulsory presence of an epoxy curing agent in the compositions described in document (2), and the use of a glycidyl ester together with an acrylate or methacrylate monomer in document (3).

6. As far as Claims 10 and 11 are concerned, which refer to curable adhesive systems containing a curing agent together with a composition according to Claims 5 to 9, the novelty of their subject matter results directly from that of the compositions.

6.1 The graft polymers disclosed in document (1) can be used with polyamidoamines as curing agent in adhesive compositions (page 8, lines 7 to 9). These polymers, as shown above, always differ from the polymers used according to Claims 10 and 11 by a lower grafting rate and a lower molecular weight; furthermore their preparation always involves the use of an unsaturated carboxylic acid as comonomer which is only optional in the present application.

6.2 As to the compositions according to document (2), they do not contain as such the mixture of a polymer composition and an epoxy curing agent, but

- either a first component consisting of the epoxy resin and the curing agent and a second component consisting of the monomer mixture, the cross-linking agent and the initiator (example 1 and Claim 8),

- or a first component consisting of the epoxy resin, the cross-linking agent and the initiator and a second component consisting of monomer mixture and the curing agent (example 2 and Claim 9).

In both cases polymerization as well as hardening and cross-linking reactions can thus occur simultaneously by simple heating which results in a complex mechanism (page 4, line 29 to page 5, line 7) necessary to achieve the bonding between rotor and strator (page 1, lines 1 to 6).

Neither of these embodiments corresponds to a binary system as claimed in Claims 10 and 11 of the application, so that novelty can be acknowledged.

6.3 The glycidyl ester copolymers described in document (3) are used in moulding applications (page 1, column 1, paragraph 1) which do not fall within the scope of claim 10 and 11.

7. There is no indication in the examination file that the Examining Division pronounced on any aspect other than novelty. In order not to deprive the Applicant of his right to a second instance, the Board considers it appropriate to remit the case to the Examining Division under Article 111(1) EPC for further prosecution in relation to issues other than novelty.

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 for further examination on the basis of the claims submitted during oral proceedings and set out in paragraph VII above.

The Registrar: The Chairman:

F.Klein K.Jahn