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D E C I S I O N
of 2 May 2000

Case Number: T 0180/98 - 3.3.3

Application Number: 93925132.8

Publication Number: 0668886

IPC: C08J 5/06

Language of the proceedings: EN

Title of invention:

Aqueous size for fiber reinforced high temperature composites

Applicant:

E.I. DU PONT DE NEMOURS AND COMPANY

Opponent:

-

Headword:

-

Relevant legal provisions:

EPC Art. 54(1), 56, 111(1)

Keyword:

"Novelty - prior disclosure - implicit feature (no)"

"Inventive step - departure from prior art teaching"

Decisions cited:

-

Catchword:

-



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Boards of Appeal

Chambres de recours

Case Number: T 0180/98 - 3.3.3

D E C I S I O N
of the Technical Board of Appeal 3.3.3
of 2 May 2000

Appellant: E. I. Du Pont De Nemours and Company
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Wilmington
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Representative: Abitz, Walter, Dr.-Ing.
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Decision under appeal: Decision of the Examining Division of the
European Patent Office posted 23 September 1997
refusing European patent application
No. 93 925 132.8 pursuant to Article 97(1) EPC.

Composition of the Board:

Chairman: C. Gérardin
Members: A. Däweritz
J. De Preter

Summary of Facts and Submissions

I. European patent application No. 93 925 132.8 filed on 5 November 1993, claiming priority of 12 November 1992 of an earlier application in the United States of America (07/989483) and published under No. 0 668 886 corresponding to WO-A-94/11419 (26 May 1994), was refused by a decision issued in writing on 23 September 1997. The decision was based on a set of three claims, Claim 1 filed on 21 May 1997 reading as follows:

"1. A stable aqueous size composition for fiber used to reinforce high temperature composites consisting essentially of as a first component, at least 0.1% by weight of a poly(amide-acid) formed from a dianhydride selected from the group consisting of 2,2-bis(3',4'-dicarboxyphenyl) hexafluoropropane dianhydride, pyromellitic dianhydride, biphenyl dianhydride, oxydiphthalic dianhydride and benzophenone dianhydride and an aromatic diamine selected from the group consisting of paraphenylene diamine, metaphenylene diamine, 4,4'-oxydianiline and 3,4'-oxydianiline, said poly(amide-acid) having been neutralized with ammonia and/or amines, as a second component, an aprotic solvent selected from the group consisting of N-methylpyrrolidone, dimethylacetamide, diglyme, dimethylformamide, and dimethylsulfoxide, said solvent being present in an amount by weight at least half that of the poly(amide-acid) and as a third component, at least 85% by weight of water."

Claims 2 and 3, which had not been amended, read as follows:

"2. A sizing composition according to Claim 1 wherein

the molar ratio of dianhydride to diamine reactant ranges between 0.8 to 1.2.

3. A size composition according to Claim 1 wherein the dianhydride reactant is 2,2-bis(3',4'-dicarboxyphenyl) hexafluoropropane dianhydride and the diamine reactant is a 95:5 mixture of para- and metaphenylene diamine."

II. In substance, the Examining Division took the view that the claimed subject-matter according to Claims 1 and 2 was not novel over FR-A-2 646 179 (D1), because

- (i) D1 disclosed sizing compositions for carbon fibers comprising a polyamide-acid which had been neutralised with amines, an aprotic solvent (for example dimethylformamide, diglyme) and water. The same starting compounds (i.e. dianhydride and aromatic diamines) were used for the manufacture of the polyamide-acids in D1 and in the application (D1: page 3, line 1 to page 5, line 11 and page 9, line 16 to page 16, line 23).
- (ii) The presence of surfactants was not essential in the aqueous coating compositions disclosed in D1 (page 14, lines 5 to 7; page 15, lines 1 to 4; Claim 12).
- (iii) The modification of Claim 1, e.g. the replacement of the word "comprising" by "consisting essentially of" did not overcome the above objection of lack of novelty raised in a previous communication, because D1 did not require the presence of surfactants either, so that a decision to refuse the application could be

issued (Article 113(1) EPC).

III. On 21 November 1997, a Notice of Appeal was lodged by the Appellant (Applicant) against this decision. The prescribed fee was paid on the same date. The Appellant requested that the decision under appeal be set aside, alternatively that oral proceedings be scheduled.

In the Statement of Grounds of Appeal filed on 30 January 1998, the Appellant argued essentially as follows:

- (i) Although D1 might give the impression that surfactants were not essential to the process disclosed, there was in fact no way to rework that teaching without the presence of a surfactant. Contrary to the reasoning in the decision under appeal, the passages of D1 referred to (Claim 12) required the presence of surfactants as an essential component of the known aqueous oiling compositions. The oiling compositions had to be dispersed by any known dispersing means to obtain aqueous oiling compositions. The only dispersing means disclosed or suggested therein was stirring the oiling composition in a solution of water and a surface active component formed from one or more surfactants, e.g. including an amphoteric and a nonionic surfactant.

- (ii) The statement in the decision under appeal that the rewording of Claim 1 by replacing the term "comprising" by the expression "consisting essentially of" would not render the Claims 1 and 2 novel over D1 was erroneous, because the

presence of surfactants was essential to the compositions disclosed in D1.

(iii) The new wording of Claim 1 expressly excluded aqueous coating (or oiling) compositions requiring the presence of surfactants. This exclusion was essential, since the aqueous oiling compositions of D1 were subject to degradation due to the presence of surfactant residuals at the high temperatures at which the coating compositions were stably used. As D1 was silent on how to make compositions without a surfactant, the claimed subject-matter also involved an inventive step.

(iv) The Appellant further requested that the appeal fee be refunded, because the Examining Division had not examined the case with adequate diligence and patience. Namely, the Applicant's arguments regarding the disclosure of D1 had not been dealt with by the Examining Division.

IV. On 18 and 20 January 2000, the Rapporteur held consultations by telephone with the professional Representative of the Appellant to discuss (i) some discrepancies between the claims on file and the arguments presented by the Appellant in the course of the examination proceedings, and (ii) the question whether all the features essential to define the invention were specified in the independent claim.

V. In a letter received on 28 February 2000, which confirmed the results of a further consultation by telephone on 25 February 2000, in which the Appellant had expressed the wish to reach a decision in writing,

the request for refund of the appeal fee was withdrawn and a new Claim 1 was submitted which reads as follows:

"1. A stable aqueous size composition for fiber used to reinforce high temperature composites consisting essentially of as a first component, at least 0.1% by weight of a poly(amide-acid) formed from a dianhydride selected from the group consisting of 2,2-bis(3',4'-dicarboxyphenyl) hexafluoropropane dianhydride, pyromellitic dianhydride, biphenyl dianhydride, oxydiphthalic dianhydride and benzophenone dianhydride and an aromatic diamine selected from the group consisting of paraphenylene diamine, metaphenylene diamine, 4,4'-oxydianiline and 3,4'-oxydianiline, said poly(amide-acid) having been completely neutralized with ammonia and/or amines selected from the group of primary, secondary and tertiary aliphatic C₁-C₄ alkyl and C₁-C₄ alkanol amines, as a second component, an aprotic solvent selected from the group consisting of N-methylpyrrolidone, dimethylacetamide, diglyme, dimethylformamide, and dimethylsulfoxide, said solvent being present in an amount by weight at least half that of the poly(amide-acid) and as a third component, at least 85% by weight of water."

VI. The Appellant requested that the decision under appeal be set aside and that a patent be granted on the basis of Claim 1 as submitted on 28 February 2000 and Claims 2 and 3 as originally filed, alternatively that oral proceedings be scheduled.

Reasons for the Decision

1. The appeal is admissible.
2. *Procedural matter*
 - 2.1 Since, as will appear hereinafter, the Appellant's main request is successful, the auxiliary request for oral proceedings can be disregarded and the issuance of a decision on the basis of the written submissions is possible (Article 113(1) EPC).
 - 2.2 Although the ground of refusal of the application was lack of novelty of the claimed subject-matter with respect to the disclosure of D1, the examination of the file reveals that the issue of inventive step had been considered before (cf. communication of 21 May 1996 and reply of 20 November 1996). To that end, the teaching of EP-A-0 330 821 (D2), corresponding to US-A-4 923 752 cited in the application in suit, had been combined with D1.

From the result of the consultation by telephone of 18 January 2000 between the Rapporteur and the Appellant's Representative, wherein reference to the above reply was made, it is evident that the present wording of the claims encompasses a combination of features essential for both a proper definition of the invention and the achievement of the desired result. This means that the claims on which the present decision is based have been drafted with a view on the requirements of not only novelty, but also clarity and inventive step.

In view of this fact and the Appellant's request that a patent be granted on the basis of these claims, the Board has decided not only to examine the question of novelty, but to make use of its power pursuant to Article 111(1) EPC and to deal itself with the issue of inventive step.

3. *Wording of the claims*

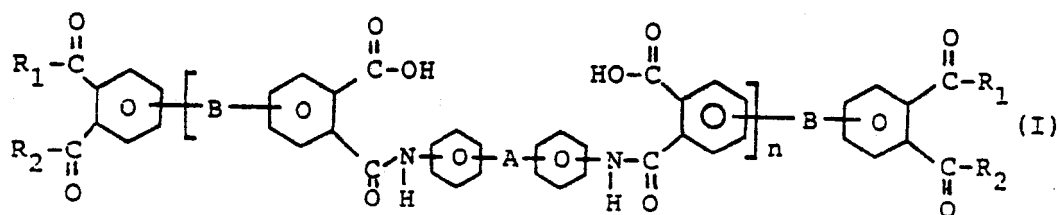
The Board is satisfied as regards the requirements of Article 123(2) EPC, because the additional features in Claim 1 are based on page 3, lines 5 to 11, 23 to 25, 29 and 30 of the application as originally filed.

No objections were raised by the Examining Division with respect to Article 84 EPC. The Board does not find the claims objectionable in this respect either, since the amendments are clear, concise and supported by the description.

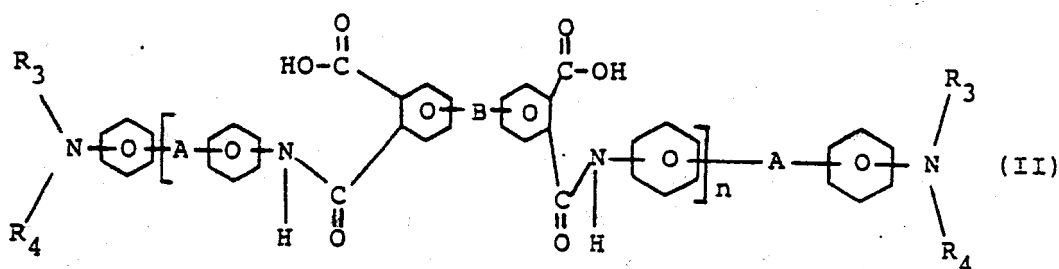
4. *Prior art*

- 4.1 D1 concerns a sizing composition for carbon fibers, which comprises at least one sizing agent selected from oligomeric polyamic acids according to formulae (I) or (II) and products being the result of partial or total imidation of such acids (Claim 1; page 10, lines 22 to 27). The compositions may be in the form of a solution in a solvent or a mixture of solvents (Claim 11) or in the form of aqueous suspensions of these sizing agents (Claim 12).

4.1.1 In the formulae (I) and (II)



and



the symbols have the following meanings:

A is a divalent radical of the formula
 $-X-[Ar_1-Z_1-Ar_1-X]_v-$ in *meta*- or *para*-position with respect to the $-NR_3R_4$ group or the $-NH-CO-$ group,

B is a divalent radical of the formula
 $-Y-[Ar_2-Z_2-Ar_2-Y]_w-$ in *meta*- or *para*-position with respect to the $-CO-R_1$ group or the $-NH-CO-$ group,

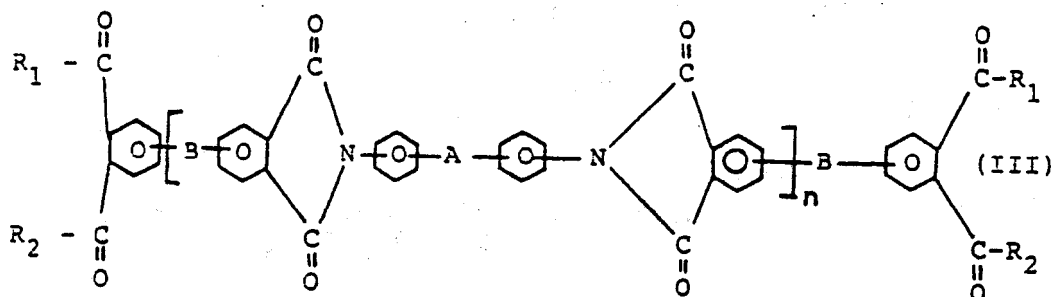
R_1 denotes a group corresponding to $-OH$, $-OR_5$ or R_5-NH- ,

R_2 represents a group corresponding to $-OH$, $-OR_5$, or R_1 and R_2 together form a divalent group $-O-$ or $R_5-NH<$,

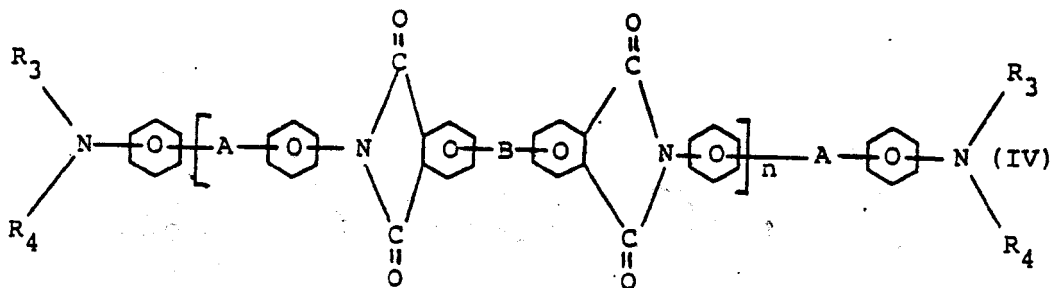
R_3 has the meaning of H or a group R_6 ,

- R_4 denotes H, a group R_6 or a monovalent group R_6 -CO-, or R_3 and R_4 together form a divalent group -CO- R_7 -CO-,
- R_5 is a monovalent organic group which does not react with an identical group or with a -COOH group,
- R_6/R_7 each represents mono- or divalent organic groups which do not react with an identical group or with a -COOH group,
- X at each occurrence denotes independently from each other -O-, -S-, -SO₂- or -CO-,
- Y at each occurrence denotes independently from each other -O-, -S-, -SO₂- or -CO- or -C_mC_{2m}-,
- Z_1/Z_2 at each occurrence represent a simple bond between two carbon atoms or a divalent group selected from the groups Y,
- Ar_1/Ar_2 each denotes substituted or unsubstituted divalent aromatic groups, which may independently from each other be the same or different at each occurrence,
- m is an integer of from 1 to 8,
- n is a number from 1 to 30 and
- v/w each represents independently from each other 0 or 1. (page 3, line 1 to page 5, line 11 and Claim 1).

The polyimides derivable therefrom correspond to formulae (III) and (IV) (page 8, line 14 *et seq.*)



and



wherein the meanings of the various groups are the same as listed above.

The products of partial imidation within the ambit of D1 comprise terminal groups containing the substituents (CO-R₁)/(CO-R₂) and -NR₃R₄, respectively, and internal units which correspond to the units shown in the brackets in both the formulae (I) and (III) and in both the formulae (II) and (IV), respectively (page 9, line 16 to page 10, line 21).

- 4.1.2 The only specific combinations of the above groups and indices **A** to **w** as defined in any one of formulae (I) to (IV) are disclosed in the examples. They include a number of combinations of distinct monomers:
 benzophenone 3,3',4,4'-tetracarboxylic acid dianhydride (**BTDA**) and bis-2,2-[4-(*p*-aminophenoxy)phenyl] propane

(**BPA**) (Example 1, Runs A and B); BPA and bis[4-(3,4-dicarboxyphenoxy)phenyl] sulphide dianhydride (**SDA**) (Example 1, Runs D, E and F); and BPA and bis(4-(*p*-aminophenoxy)phenyl sulphone (**SED**) (Example 1, Run G).

Some of the poly(amide-acids) obtained from these combinations were partially modified by reaction with phthalic acid anhydride (Example 1, Runs C and D) or directly converted into polyimides (Example 1, Runs E, F and G) before further treatment with a solvent and, optionally, water (Example 2; page 23, lines 32 to 39; the table on page 26).

4.1.3 In accordance with a preferred embodiment, the sizing agents are chosen from compounds of the formula (I) or (II) (page 10, lines 28 to 31) prepared from a diamine and an dianhydride or the corresponding tetracarboxylic acid at ambient temperature or close to this temperature in an aprotic polar solvent. An amine R_5-NH_2 , such as aniline, may be added to the reaction mixture in order to neutralise the dicarboxylic or anhydride terminal groups of the polymeric chains according to formula (I) by forming neutral terminal groups of the structures:



(page 10, line 32 to page 11, line 23), i.e. acidic semi-amide or neutral imide groups.

According to page 11, line 24 to page 13, line 13 the compounds of formula (II) are prepared and optionally modified in a similar way (cf. Example 1, Runs C and D, and point 4.1.2).

4.1.4 The list of suitable aprotic polar solvents disclosed on page 13, lines 14 to 20 encompasses all the solvents used in accordance with the application in suit (cf. page 2, lines 14 to 16).

4.1.5 According to a preferred embodiment, the sizing composition is in the form of a suspension of the sizing agent(s) in aqueous phase (cf. page 14, line 1 to page 15, line 4, Claim 12). It may be prepared from a product in powder form or in solution by means of any known dispersing method.

In particular, a solution of the sizing agent in an appropriate solvent can be dispersed with stirring in a suitable amount of water containing 0.05 to 2.5% by weight of a surfactant component comprising one or more surfactants. The solids content and the amount of the solution to be dispersed into the water are specified. However, these details do not allow to calculate the water content in the resulting suspension to be at least 85% by weight (page 14, lines 5 to 23).

4.1.6 The surfactant component is defined on page 14, last paragraph (cf. Claims 13 to 15 as well) and the agitation necessary to prepare the suspension is referred to on page 15, lines 1 to 4. That agitation may be achieved by means of any mechanical stirring system providing effective shear of the droplets of the solution to be dispersed in water.

4.1.7 In all the dispersions of Example 2, 20 parts by weight of solution are dispersed in 100 parts by weight of water containing 0.5% of surfactant agents, resulting in a suspension containing 83% by weight of water (page 24, lines 8 to 16).

4.2 The sizing composition of D2 comprises a polymerised perfluorinated poly(amide-acid) in a mixture of (i) an aprotic solvent selected from dimethyl sulphoxide, dimethyl formamide, diglyme and N-methylpyrrolidone (**NMP**), and (ii) an alcohol selected from methanol, isopropanol and ethanol, the weight ratio of the aprotic solvent to the alcohol being 1:4 to 1:20 (Claim 1). The preferred polymer is prepared by a substantially stoichiometric reaction of 2,2-bis(3',4'-dicarboxyphenyl) hexafluoropropane dianhydride and a mixture of para- and meta-phenylene diamine in a ratio of about 95:5 in NMP (column 2, lines 4 to 8; Example).

5. Novelty

5.1 D1 does not disclose a poly(amide-acid) formed from a combination of a dianhydride selected from a list of five specific compounds and an aromatic diamine selected from a list of four specified compounds, which polymer has been completely neutralised with ammonia and/or primary, secondary or tertiary aliphatic C₁-C₄ alkyl or C₁-C₄ alkanol amines.

Moreover, it is silent with respect to the absence of any surfactant and the amount of water to be used in the dispersion in accordance with the preferred embodiment disclosed on page 14. From the amounts of the ingredients used in Example 2 (page 24, lines 8 to 16), the water content can be calculated as being 83%

by weight, i.e. less than 85% as required in Claim 1 of the application in suit.

5.2 D2 differs from the composition as claimed in that a particular mixture of aprotic solvents and alcohol in a specific weight ratio is used, but no water.

5.3 It follows that the subject-matter of Claim 1 is novel with respect to both citations.

6. *Problem and Solution*

6.1 The patent application in suit concerns an aqueous size for fiber reinforced high temperature composites.

6.2 An aqueous sizing composition for carbon fibers is known from D1, which is considered by the Board to represent the closest state of the art.

6.2.1 This composition comprises at least one sizing agent selected from oligomeric poly(amide-acids) and products obtainable therefrom by partial or total imidation (Claim 1), a solution of which in a polar aprotic solvent may be dispersed in an aqueous medium in accordance with a preferred embodiment (cf. points 4.1 to 4.1.7, *supra*). When used in the form of aqueous suspensions, the compositions comprise a mixture of an ethoxylated nonylphenol and a "fatty-chain" betaine (page 24, paragraph 2); alternatively they are used as organic solutions (page 24, paragraph 1).

6.2.2 This known composition aims at improving the interfacial adhesion between fibers and the matrix in fiber-reinforced polymer composites as well as the resistance against aging due to thermal and moisture

attacks (page 2, lines 9 to 31). However, as reported in the introduction of the application in suit (page 1, lines 26 to 33), it is difficult to control the size concentration in an application bath comprising such a mixture of aprotic solvent and alcohol and, consequently, the yarn size pickup, because the alcohol evaporates easily; furthermore the size requires that certain precautionary measures be taken in handling both from the standpoint of safety and with regard to environmental considerations.

- 6.3 In view of these shortcomings and in line with this introductory statement, the technical problem underlying the patent application in suit may thus be seen as the provision of a stable highly diluted aqueous sizing composition which contains only limited amounts of solvent and thus obviates or reduces the difficulties of solvent based systems, such as concentration control and environmental difficulties, but which gives results comparable to the products of those systems and does not give rise to problems due to the presence of additional components.
- 6.4 According to the patent application in suit, the technical problem has been solved by a stable aqueous size composition consisting essentially of a poly(amide-acid), an aprotic solvent and water, as specified in Claim 1.
- 6.5 As shown in the examples of the application, the results obtained with such stable aqueous sizing compositions are at least equivalent to those achieved with non-aqueous (solvent-based and surfactant-free) sizing agents or to commercial sizes based on epoxy resins. Thus, uniform coating (e.g. coefficients of

variation of less than 8.5), satisfactory to good dynamic friction characteristics, values of stiffness, cohesion of coated fibers and processing characteristics of yarns treated with the size are reported. Consequently, the above defined technical problem is effectively solved.

7. *Obviousness*

It remains to be decided whether this solution was obvious to a person skilled in the art having regard to the state of the art available to and relied upon by the Examining Division.

7.1 The various embodiments disclosed in D1 would not provide an incentive for a skilled person to consider a solution along the line of the claimed subject-matter.

7.1.1 First, it is evident from the above considerations with respect to novelty that D1 discloses a vast range of polymers encompassed by formulae (I) to (IV). Although, by an appropriate selection of substituents and indices in these formulae, it might be possible to define a polymer meeting the requirements of the first component in Claim 1, there is however no suggestion in D1 to make such a selection. In fact, even if the poly(amide-acids) defined by a specific formula had been selected, the essential feature would be the presence of inert groups, which should prevent any further polycondensation caused by the high temperatures at which the size compositions are used (page 2, lines 23 to 31).

7.1.2 Moreover, the document does not require an aqueous system and, consequently, cannot suggest to prepare a

stable composition containing at least 85% by weight of water. Furthermore, it is totally silent about the possibility to completely neutralise the polymer with ammonia and/or a short-chain, hence easily volatilisable amine as specified in Claim 1, in order to achieve partial depolymerisation and hydrolysis to molecular sizes which are then micro-emulsified and solubilised in water (cf. application in suit, page 3, lines 22 to 32).

- 7.1.3 It is not derivable from the document either that these features would allow to dispense with surfactants, but, nevertheless, to prepare a stable micro-emulsion, and that the polymer would repolymerise upon heating without affecting the desirable properties of the fibers treated with the size (cf. application, page 4, lines 11 to 17).

As explained in the application in suit (page 2, last paragraph), sizing compositions are generally required to be capable of forming a coating on the fiber, which should be as continuous and uniform as possible, in order to provide improved handleability of the yarn during processing and to assure uniform contact with the matrix polymer. At the same time it should resist high temperature degradation during formation of the composite which could interfere with adhesion to the matrix polymer.

Therefore the Board accepts the Appellant's argument that the presence of surfactants would be undesirable in order "to avoid degradation of the micro-emulsion at the high temperatures in which such micro-emulsion was designed to perform due to the presence of surfactant residuals." (Statement of Grounds of Appeal, page 3,

point 4).

7.1.4 Hence, the Board cannot see any suggestion in D1 to arrive at something falling within the terms of Claim 1 in order to solve the above technical problem, by selecting specific polymers, neutralising them completely with specific bases and forming a stable aqueous composition of these three components.

7.2 The Board does not see any incentive in D2 in this respect either, which requires the preparation of organic solutions of sizing agents in a combination of polar solvents and alcohol. The document does not provide any teachings with respect to the preparation of stable aqueous sizing compositions nor that poly(amide-acids) could be used therefor.

The mixture of aprotic solvent and alcohol must in fact be regarded as the essential teaching of D2. As explained in the introduction of that citation (column 2, lines 12 to 31), it is generally not desirable to use a poly(amide-acid) in an aprotic solvent alone for several reasons, in particular because this would not yield the desired thin, continuous uniform coating on the carbon fiber and because substantial amounts of solvent would have to be removed after curing of the polymer. The dilution of the aprotic solvent with a low molecular weight alcohol serves several purposes, in that the alcohol lowers the surface tension of the solution, causes no precipitation of the polymer and offers a high vapour pressure for ease of removal during curing of the thread line. In the Board's view, a skilled person faced with the above-defined technical problem had thus no incentive to depart from that teaching and, thereby,

forgo the advantages provided by the alcohol in order to consider aqueous systems which are not mentioned.

- 7.3 It follows that the stable aqueous size composition as claimed would not be obvious to a skilled person having regard to the state of the art considered by the Examining Division, whether considered in isolation or in combination and, therefore, it involves an inventive step.
8. Claims 2 and 3, which relate to preferred embodiments of Claim 1, are supported by the patentability of the main claim and thus also allowable.
9. Although the claims on which the present decision is based meet the formal and substantive requirements of the EPC, a patent cannot be granted according to the Appellant's request, because the description has still to be adapted to the new wording of the claims. To that end the case has to be remitted to the Examining Division with the order to grant on the basis of the claims discussed above, after adaptation of the description.

Order

For these reasons it is decided that:

1. The decision under appeal is set aside.
2. The application is remitted to the Examining Division with the order to grant a patent on the following basis:

- Claim 1 as submitted on 28 February 2000
- Claims 2 and 3 as originally filed
- A description yet to be adapted to these claims.

The Registrar:

The Chairman:

E. Görgmaier

C. Gérardin