Case Number: T 0663/97 - 3.3.3
Application Number: 93309946.7
Publication Number: 0604074
IPC: C08L 67/02
Language of the proceedings: EN
Title of invention: Stabilization of polybutylene terephthalate/polyester blends
Applicant: GENERAL ELECTRIC COMPANY
Opponent: -
Headword: -
Relevant legal provisions: EPC Art. 54, 56, 84
Keyword: "Claims - clarity (yes)"
"Novelty - prior disclosure - implicit features (no)"
"Inventive step - non-obvious combination of known features"
Decisions cited: -
Catchword: -
Case Number: T 0663/97 - 3.3.3

DECISION
of the Technical Board of Appeal 3.3.3
of 15 December 2000

Appellant: GENERAL ELECTRIC COMPANY
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Representative: Goode, Ian Roy
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Decision under appeal: Decision of the Examining Division of the European Patent Office posted 21 January 1997 refusing European patent application No. 93 309 946.7 pursuant to Article 97(1) EPC.

Composition of the Board:
Chairman: C. Gérardin
Members: B. ter Laan
A. Lindqvist
Summary of Facts and Submissions

I. European patent application No. 93 309 946.7, filed on 10 December 1993, claiming priority of 22 December 1992 from an earlier application in the USA (US 994738) and published on 29 June 1994 under No. 0 604 074 (Bulletin 94/26) was refused by a decision of the Examining Division of the European Patent Office dated 21 January 1997. That decision was based on a set of ten claims filed on 9 May 1996, Claim 1 reading:

"A thermoplastic resin blend comprising:
(a) a relatively low molecular weight polybutylene terephthalate resin having a melt viscosity of less than 450 poise;
(b) a relatively high molecular weight polyester resin having a melt viscosity greater than 900 poise; and
(c) an effective melt viscosity stabilizing amount of a stabiliser selected from acidic phosphate salts, Group 1B metal phosphate salts and Group IIB metal phosphate salts."

Dependent Claims 2 to 10 referred to preferred embodiments of the thermoplastic resin blend according to Claim 1.

II. The refusal was based on the following documents:

D6: US-A-4 532 290,

D7: GB-A-1 466 154,

D8: WO-A-92/07026 and

The Examining Division held that the claimed subject-matter did not satisfy the requirements of Article 54 EPC. In particular, it was found that the polyester component (b) of the claimed composition also comprised polybutylene terephthalate and that the difference in molecular weight as indicated could not serve to distinguish the claimed blend over conventional polybutylene terephthalate resins, since all such resins consisted of fractions having different molecular weights. Therefore, all documents describing mixtures of polybutylene terephthalate with an acidic phosphate salt destroyed the novelty of the claimed subject-matter.

Although obviousness did not form part of the grounds for refusal in view of the novelty objection, it was pointed out that it was known to add the present stabilizers to polybutylene terephthalate in order to improve the melt stability, which was the object of the application in suit.

III. On 20 March 1997 a Notice of Appeal was lodged against that decision, together with payment of the prescribed fee. The Statement of Grounds of Appeal, filed on 2 June 1997, was based on a newly filed main request having 25 claims and a first auxiliary request of 22 claims.

With a letter dated 19 May 2000, a second and a third auxiliary request were filed, having 25 and 4 claims, respectively.

IV. During the oral proceedings, held on 26 May 2000, after discussion of the claims then on file, a new main request of 24 claims was submitted and the previous
third auxiliary request (25 claims) was maintained as the sole auxiliary request. Claim 1 of the main request reads:

"A thermoplastic resin blend comprising:
(a) from 5 to 95 parts by weight of a relatively low molecular weight polybutylene terephthalate resin having a melt viscosity of less than 450 poise as measured using a Tinium Olsen melt indexer at 250°C, 0.042 inch orifice (ASTM method D1238) or having an intrinsic viscosity of above 0.45 decalitres/gram as measured using a 120-130 mg sample in a 3:2 mixture of phenol/tetrachloroethane and measuring the time of flow with a Ubbelohde capillary viscometer at 25°C;
(b) from 5 to 95 parts by weight of a relatively high molecular weight polyester resin having a melt viscosity greater than 600 poise as measured using a Tinium Olsen melt indexer at 250°C, 0.042 inch orifice (ASTM method D1238) or having an intrinsic viscosity of above 0.6 decalitres/gram as measured using a 120-130 mg sample in a 3:2 mixture of phenol/tetrachloroethane and measuring the time of flow with a Ubbelohde capillary viscometer at 25°C; the amounts of (a) and (b) being based on a total of 100 parts by weight of (a) and (b) and
(c) from 0.1 to 10 weight percent based on the weight of the total composition of (i) an acidic phosphate salt, (ii) an acid, alkyl, aryl or mixed phosphite having at least one hydrogen or alkyl group, or (iii) a Group IB or IIB metal phosphate salt, (iv) a phosphorous oxo acid or (v) a mixture of any of the foregoing."
Dependent Claims 2 to 17 refer to preferred embodiments of the thermoplastic resin blend according to Claim 1. Claim 18 concerns an article prepared from compositions as defined in Claim 1. Claim 19 is directed to a process for stabilizing the melt viscosity of a thermoplastic resin blend according to Claim 1. Dependent Claims 20 to 23 refer to preferred embodiments of the process of Claim 19.

Claim 24 is a further claim directed to a thermoplastic resin blend consisting essentially of the above compounds (a) to (c) and, optionally, one or more of a thermoplastic polymer additive (d), a reinforcing agent (e), a flame retarding agent (f) and a conventional additive (g).

V. Concerning the wording and the patentability of these claims the Appellant argued as follows.

(i) The amendments were adequately supported by the original application.

(ii) Since the introduction of the measuring method used to determine the melt viscosity evoked questions by the Board (Article 84 EPC) which the representative was not in a position to answer without the support of a technical expert, it was decided to leave those questions open. Accordingly, the Appellant was invited to clarify in writing the methods used to measure and the units used to indicate the molecular weights of the polymers and to indicate the meaning of the various viscosities, in particular poise Kayness, expressed in the examples.
(iii) Regarding novelty and inventive step, the difference between a blend and a single resin could be seen from the difference in melt stability with time and temperature, as demonstrated in Figures 1 and 2 of the application. The increase in melt viscosity over time shown by the blend posed a problem not encountered with single resins. The solution to that problem, as defined in the claims, was not suggested by the prior art since no document described polybutylene terephthalate/polyester blends and the documents disclosing the use of stabilizers concerned different problems.

(iv) Thereafter, the discussion of the substantive issues was closed.

VI. In its submissions of 21 August 2000 and 9 November 2000 the Appellant explained that (i) although the method mentioned in the claim resulted in different units than those indicated in the claim, the skilled person could, on the basis of the information contained in the application, convert those units, and (ii) the ASTM-D3835 provided the basis for the Kayness test.

VII. The Appellant requests that the decision under appeal be set aside and that a patent be granted on the basis of Claims 1 to 24 submitted as the main request during oral proceedings, alternatively on the basis of the set of claims labelled "Third auxiliary request" submitted on 19 May 2000.

Reasons for the Decision
1. The appeal is admissible.

Main request

Article 123(2) EPC

2. The amendments to the claims are in conformity with the requirements of Article 123(2) EPC.

Claims 1 and 19 differ from the ones as originally filed in that

(a) the amounts of the polymers are now specified, support for which can be found on original page 8, lines 17 to 30,

(b) the melt viscosity is indicated, based on original Claims 3 and 4 as well as page 4, lines 2 to 11,

(c) the method of measuring the melt viscosity is indicated, disclosed on original page 1, lines 26 to 29, and original page 2, lines 4 to 10,

(d) the amount of phosphorus-containing compound (c) is specified, which is based on original page 9, lines 26 to 32, and

(e) the intrinsic viscosity of the polymers is indicated. The intrinsic viscosity of 0.6 decaliters/gram as measured using a 120-130 mg sample of polyester in a 3:2 mixture of phenol/tetrachloroethane and measuring the time of flow with a Ubbelohde capillary viscometer at 25°C was disclosed as an alternative to a melt
viscosity of above about 600 poise as measured using a Tinium Olsen melt indexer at 250°C, 0.042 inch orifice (ASTM method D-1238) (original page 1, lines 29 to 33). In this respect, the Appellant stated during the oral proceedings that this alternative definition could be derived from the melt viscosity and was valid for all the polymers of the application in suit.

Clarity and support

3. The introduction in the claims of the measuring method for the melt viscosity gave rise to a number of questions by the Board, which were answered in writing after the oral proceedings. Those questions concerned the units and the measuring methods of the various viscosities used to define the polymers of Claims 1 and 6.

3.1 The first question concerned the method and units used to measure the molecular weight as indicated by the melt viscosity of the polymers.

3.1.1 In D8, page 8, lines 9 to 16, and in Example 1 (Table 1), the molecular weight of polyesters is indicated by their intrinsic viscosities, expressed in dl/g as measured in a 60:40 phenol tetrachloroethane mixture at 30°C. In Examples 25 to 27 (Table 4) the melt viscosity of a blend of polymers and various additives is expressed in poise. In D9 polymers are indicated by their melt viscosity, expressed in poise (Example 1: polyphenylene sulphide), by their melt index, expressed in g/10 min (Example 2: polyetherimide, measured at an orifice of 0.0825 inch diameter; Examples 3 and 5: polycarbonate, measured by
method ASTM-D-1238, condition O), or by their intrinsic viscosities, expressed in dl/g (Example 5: polybutylene terephthalate).

As can be seen from D8 and D9, molecular weights of polymers can be indicated by their intrinsic viscosities (dl/g). The ASTM-D-1238 method gives a result expressed in g/10 min, whereas the melt viscosity is expressed in poise.

In present Claims 1 and 19 the molecular weights of the polyesters are indicated by their melt viscosities (poise), measured according to ASTM-D-1238 (g/10 min).

According to the Appellant's written explanations, the method ASTM-D-1238 made a one point measurement at a single shear rate for determining melt flow, expressed in g/10 min. This melt flow was inversely proportional to the melt viscosity in poise. The proportionality constant was dependent on the geometry of the machine being used (orifice diameter, length of capillary, diameter of barrel) and the density of the polymer being tested. It could be established by running a standard sample having a known viscosity and measuring the melt flow rate in g/10 min.

The Appellant also referred to method ASTM-D-3835, which described the way to calculate the viscosity for Newtonian systems as well as the apparent viscosity for non-Newtonian systems, which specific relationship could also be used to convert melt flow to viscosity for a given density of the polymer.

According to the Appellant, the molecular weight was related to both the melt viscosity and the melt flow,
but it was measured using gel permeation chromatography. It was possible to develop a correlation for a range of molecular weights and viscosities, as well as the relationship between the molecular weight and the intrinsic viscosity, which was measured in solution.

3.2 The second question concerned the meaning of the various viscosities expressed in the examples, in particular poise Kayness. In its letter of 31 August 2000, the Appellant referred to method ASTM-D-3835, which also formed the basis for the Kayness test.

3.3 In view of the disclosure in the application in suit, which gives details of the machines used for measuring the melt flow (page 1, lines 27 to 29; Claim 1) and the Kayness viscosity (page 15, lines 9 to 17), the Board takes the view that the molecular weights of the resins are appropriately defined, so that the requirements of Article 84 EPC are considered to be fulfilled.

Novelty

4. The novelty objection of the Examining Division was based on the lack of difference between a single polybutylene terephthalate resin as described in D6 to D9, and a mixture of two such resins having different molecular weights.

4.1 D6 describes a thermoplastic resin composition comprising:

(a) 100 parts by weight of an aromatic polycarbonate resin;
(b) 5 to 95 parts by weight of at least one polyester resin prepared by reacting terephthalic acid or a reactive derivative thereof and an alkane diol; and

(b) a melt-stabilizing amount of monosodium phophate, monopotassium phosphate or a mixture thereof (Claim 1). The polycarbonate resin (a) may be poly(bisphenol A carbonate) (Claim 8), the polyester resin (b) may comprise poly(1,4 butylene terephthalate) (Claim 9) or poly(ethylene terephthalate) (Claim 10), or a mixture of the two (Claim 11).

In the examples mixtures of poly(bisphenol A) carbonate and poly(1,4-butylene terephthalate), in combination with various phosphorus-containing compounds, are used to demonstrate the stabilizing effect of the latter by the higher melting points and viscosities of the mixtures as compared to control mixtures. The poly(1,4-butylene terephthalate) is identified as VALOX® 315. Although the melting points and melt viscosities of the compositions are indicated, no mention is made of their change with time, nor of any of the molecular weights or viscosities of the individual components of those compositions.

4.2 D7 discloses an aromatic polyester resin composition with inhibited colouration, which comprises:

(1) 100 parts by weight of an aromatic polyester resin derived from a glycol component at least 70 mol% of which consists of tetramethylene glycol and an acid component at least 70 mol% of which consists of isophthalic acid, terephthalic acid, a naphthalene
dicarboxylic acid, or a polyester-forming derivative thereof, which components are polymerized with a titanium compound catalyst,

(2) 5 to 100 parts by weight of a polycarbonate resin per 100 parts by weight of the aromatic polyester resin, and

(3) 0.01 to 3 parts by weight per 100 parts by weight of the aromatic polyester resin of at least one phosphorus compound which is liquid or solid at room temperature and has a specific formula (Claim 1). The aromatic polyester resin has a preferred intrinsic viscosity of 0.3 to 1.5 (page 2, lines 28 to 30), preferred polycarbonate resins have a number average molecular weight of 10,000 to 100,000 (page 2, lines 45 to 47). In the examples a poly(tetramethylene terephthalate) with an intrinsic viscosity of 0.72 is mixed with a polycarbonate of 2,2-bis(4-hydroxyethyl phenyl) propane having an intrinsic viscosity of 0.68, and various phosphorus-containing compounds.

Compositions not containing the phosphorus compounds have a marked yellowness as compared to compositions that do contain a phosphorus compound (page 7, lines 1 to 10). Furthermore, it is concluded that the colouration is not a consequence of heat degradation, but of the mixing the polycarbonate with the polyester (page 7, lines 10 to 20).

D8 describes a thermoplastic resin composition comprising:

A. from about 80 to about 15 parts by weight of a resinous composition comprising a combination of:
(a) a polyester resin having an intrinsic viscosity of at least about 0.4 deciliters/gram as measured in a 60:40 phenol:tetrachloroethane mixture at 30°C, and

(b) an effective amount of a thermoplastic elastomeric impact modifier selected from the group consisting of a copolyetherester resin, a copolyetherimide ester resin, a styrene/acrylonitrile-modified EPDM elastomer, a copolymer of an olefin and an ester of an acrylic or methacrylic acid and mixtures thereof, and, correspondingly,

B. from about 20 to about 85 parts by weight of:

(a) a filler selected from zinc oxide, barium sulphate, zirconium oxide, zirconium silicate, strontium sulphate; or

(b) a mixture of such fillers (Claim 1).

The polyesters may preferably be poly(ethylene terephthalate) and poly(1,4-butylene terephthalate) or mixtures thereof (page 8, lines 6 to 8). The intrinsic viscosity of the polyesters is at least about 0.4 dl/g, preferably at least 0.7 dl/g. An increased toughness of the composition is observed at intrinsic viscosities above about 1.1 dl/g (page 8, lines 9 to 16). Copolyetherester and copolyetherimide ester resins, in particular polyester hard block and polyester soft block-modified thermoplastic elastomers, are described as preferred impact modifiers (page 9, lines 12 to 16). Phosphites are mentioned as preferred antioxidants
other additives such as external lubricants and flame retardants may, apart from the filler material, also be present (page 23, line 22 to page 26, line 18).

In the examples a polyetherimide ester resin, a polycarbonate resin and a poly(butylene terephthalate) resin are mixed with various additives, such as zinc phosphate (Example 1). The poly(butylene terephthalate) resins are identified as VALOX 295, having an intrinsic viscosity of 0.78 dl/g at 25°C in a 60:40 mixture of phenol and tetrachloroethane (Table 1), VALOX 315, both of GE Plastics and PET grade X5202 of ICI Chemicals.

The compositions according to D8 provide highly dense thermoplastic moulded articles with improved impact strength and properties suitable to replace ceramics and filled thermosets in many applications (page 3, lines 7 to 24).

4.3 D9 describes a thermoplastic moulding composition which comprises:

(a) a resin selected from the group consisting of polycarbonates, polyethylene terephthalate and copolymers thereof, polypropylene terephthalate and copolymers thereof, polycyclohexylterephthalate and copolymers thereof, polyetherimides, polyphenylene sulphides, polyamides, polyamide imides, polyarylates, polyethersulphones, polystyrenes, polyacetals, SAN, SMA, ASA, modified polyphenylene etsers, polyether ketones, ABS, PVC, PFA, ECTFE, ETFE, PVDF and liquid crystal polymers;
(b) and from 20 - 85% by weight of total composition of a filler selected from zinc oxide, barium sulphate, zirconium oxide, zirconium silicate and mixtures thereof (Claim 1).

In Example 3 a polycarbonate is used in combination with a number of additives, amongst which Irgafos 168, which is tris(2,4-ter-butylphenyl)phosphite. In Example 5 a mixture of a polycarbonate, a polyetherimide ester elastomer and a polybutylene terephthalate (Valox 295, with an intrinsic viscosity of 0.78 at 25°C, in 60:40 mixture of phenol/tetrachloroethane) is used in combination with a number of other additives, amongst which large amounts of zinc phosphate. The compositions according to D9 may be used to prepare containers intended for use in microwave cooking (page 2, lines 17 to 18).

5. As can be seen from the above analysis of documents D6 to D9, none of them mentions a mixture of a low molecular weight polybutylene terephthalate (melt viscosity less than 450 poise) with a high molecular weight polyester (melt viscosity greater than 600 poise). The Examining Division held that one could not differentiate such a mixture from a single polybutylene terephthalate. However, in view of

(i) the statement in the description (page 2, lines 10 to 19), that blends of high molecular weight polyester and low molecular weight polybutylene terephthalate initially exhibited a decrease in melt viscosity which however increased with time, or, in other words, showed a decrease in the stability of the melt viscosity,
(ii) the difference in molecular weights of both components which, according to the Appellant's statement during the oral proceedings, gives rise to a bimodal molecular weight distribution not present in a single polyester, and

(iii) the teaching of D1 (EP-A-0 362 872) which, as will appear hereinafter, shows that blends of polybutylene terephthalate resins having different intrinsic viscosities are not equivalent to single polybutylene terephthalate polymers in that they exhibit improved thermal and mechanical properties as well as flowability in the melt,

the Board accepts that differentiation between a single polyester and a blend as defined in Claim 1 is possible.

For those reasons, the Board concludes that the subject-matter of Claim 1 is novel.

Closest document

6. The application in suit concerns stabilization of polybutylene terephthalate/polyester blends. Stabilization of polycarbonate/polyester blends is described in D6, which both the Examining Division and the Appellant considered to be the closest document.

6.1 The wording of Claims 1 and 19 on file reveals that the three features which are essential for the scope of these independent claims are the presence of (a) a low molecular weight polybutylene terephthalate, (b) a high molecular weight polyester, and (c) a phosphorus-
containing compound. The above discussion of prior art shows that D6 describes features (b) and (c), but not feature (a).

6.2 By contrast, document D1 relates to a polybutylene moulding composition consisting of at least two polybutylene terephthalate resins with substantially different molar distributions expressed by intrinsic viscosity, releasing agent for moulded products out of metal mould, heat stabilizer and with or without filler (Claim 1). According to Claim 2, the intrinsic viscosities of the two resins are between 0.70 and 0.92 and between 0.93 and 1.40 dl/g measured at 30°C in a mixture of tetrachloroethane 60 and phenol 40 both in parts by weight. As a heat stabilizer "Irganox" is used in Tables 3 and 4. No phosphorus-containing compounds are mentioned. The polymer compositions show a high flowability under moulding conditions, and they impart good thermal and mechanical properties to products made from the compositions (page 2, lines 11 to 13, 48 to 51; page 2, lines 5 to 11). Hence D1 describes features (a) and (b), but not feature (c).

6.3 Though therefore at first sight both D1 and D6 would appear to be equally relevant in that they each disclose two of the three features which determine the general properties of the present blends, the description of the application clearly invites to consider D1 as the closest document. In the introduction the object of the invention is defined as to find a high flow blend having a stable melt viscosity, this composition being based on a high molecular weight polyester resin and a low molecular weight polybutylene terephthalate resin (page 1, lines 3 to 6; page 2, lines 1 to 19). The experimental
data in the examples accordingly show the changes in melt viscosity with time of various blends within the terms of the application in suit (Examples 1 to 19) and, for comparative purposes, of a blend of high molecular weight polybutylene terephthalate and low molecular weight polybutylene terephthalate either without a phosphorous compound (Examples 1A, 4A, 5A, 6A, 7A, 8A and 14A) or with a phosphorous compound outside the scope of the present claims (Examples 6B, 6C and 7B).

Therefore, in the Board's view, there are good reasons not to depart from the approach of the application, which means that D1 qualifies as the closest state of the art.

7. As stated above, D1 describes polybutylene moulding compositions comprising at least two polybutylene terephthalate resins with substantially different molecular weight distributions. These compositions have a good balance of thermal and mechanical properties as well as a high degree of melt flowability. However, such blends show an increase of melt viscosity with time, thus limiting their use in commercial applications.

7.1 In the light of this shortcoming, the technical problem underlying the application in suit may be seen as providing a high flow polyester moulding composition having improved stability of the melt viscosity with time.

7.2 According to the application in suit that problem is solved by a composition comprising a low molecular weight polybutylene terephthalate a high molecular weight polybutylene terephthalate...
weight polyester and a phosphorus-containing compound, as specified in Claims 1 and 19.

7.3 In view of the experimental results in the examples of the application in suit, in particular the reduction of melt viscosity increase with time, the Board considers that the above defined problem is effectively solved by the combination of features according to Claims 1 and 19.

Obviousness

8. It remains to be decided whether the claimed subject-matter is obvious having regard to the documents on file.

8.1 D1 does not contain any information concerning the melt viscosity of the blends, let alone possible problems regarding that property or solutions to any such problems.

As stated above (point 6.2), additives which may form part of the compositions according to D1 are releasing agents, heat stabilizers and fillers (Claim 1, examples). None of these is a phosphorus-containing compound, nor do they serve to stabilize the melt viscosity with time. Therefore, D1 by itself does not render the claimed subject-matter obvious.

8.2 Phosphorus-containing compounds are described in D6 to D9. In D6 and D7, phosphorus-containing compounds are added to compositions comprising a polyester and a polycarbonate with the aim of melt stabilization (D6) and colouration inhibition (D7), respectively. The necessity of doing so arose from the particular
problems occurring as a consequence of transesterification reactions between polycarbonate and polyester initiated by catalytic residues in the latter (D6: column 1, lines 37 to 53) or from unspecified reactions arising from mixing those polymers (D7: page 1, lines 30 to 39; page 7, lines 15 to 20). From D6 it can be seen that the addition of monosodium phosphate, in contrast with a number of other phosphorous-containing compounds, leads to an increase in melting point and melt viscosity (Table 1), the decrease of which two properties being indicative of the degradation of at least one of the polymeric components (column 3, line 63 to column 4, line 3). D7 demonstrates the effects of several phosphorus-containing compounds on the colour of blends of polycarbonate with an aromatic polyester (Table 1 and Examples 18 and 19). Neither of the two documents addresses the problem of a stable melt viscosity with time. Accordingly, those documents do not contain any teaching regarding the influence of phosphorus-containing compounds in general on that property, let alone that on the compounds as specified in present Claims 1 and 19.

Therefore, neither D6 nor D7, taken alone or in combination with D1, would lead to the combination of features now being claimed.

8.3 The same argument is valid for D8 and D9, which both concern a mixture of polymers and a filler. Phosphites are generally mentioned as preferred antioxidants in D8 (page 26, lines 7 to 10), zinc phosphate is used in Example 5 of D9. Neither of the two documents refers to melt viscosity, so that no teaching can be inferred from them.
8.4 For the above reasons, the Board comes to the conclusion that the subject-matter of Claim 1 involves an inventive step.

9. The above considerations also apply to independent Claim 19 since its subject-matter is based on the same combination of features as in Claim 1.

10. As Claims 1 and 19 of the main request are allowable, the same goes for dependent Claims 2 to 18 as well as Claims 20 to 24, the patentability of which is supported by that of Claims 1 and 19.

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 24 submitted during the oral proceedings, after any consequential adaptation of the description.

The Registrar: The Chairman:

E. Görgmaier C. Gérardin