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(54) Title: EPOXY ADHESIVE COMPOSITION

(57) Abstract: The invention relates to an epoxy adhesive composition comprising a) a first epoxy resin, b) a second epoxy resin modified with an acrylonitrilebutadiene rubber, the latter comprising on average less than 25 wt% acrylonitrile, and c) a toughener. The total amount of component b) and component c) is higher than 30 % based on the total weight of the composition, and the weight ratio of component c) to component b) is greater than 1:1. The invention further relates to the use of said epoxy adhesive composition for the assembly of parts of a vehicle. It also relates to a vehicle, parts of which are assembled by said epoxy adhesive composition.

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Epoxy Adhesive Composition

The present invention relates to an epoxy adhesive composition according to claim 1, the use of the epoxy adhesive composition for the assembly of parts of a vehicle according to claim 13, and a vehicle according to claim 14.

Epoxy adhesive compositions are reaction adhesive compositions comprising an epoxy resin, a curing agent and usually an accelerator. Upon heat-activation, the epoxy groups of the epoxy resin react with the curing agent linking the epoxy resin compounds by a polyaddition reaction to obtain a cured product.

Such a cured product is known to have good mechanical properties and a chemical resistance superior to the cured product of other reaction adhesives. These characteristics make epoxy adhesive compositions particularly useful for demanding applications where stringent mechanical requirements must be satisfied, for example in the automotive industry.

The cured product of an epoxy adhesive other than a structural epoxy adhesive generally has a relatively high static strength, for example a high tensile and lap shear strength. Its dynamic strength however, i.e. its impact peel strength, is generally low.

Adhesives used for the assembly of parts of a vehicle, such as cars, vans, lorries, trucks and trains, are called structural adhesives. The cured product of such a structural adhesive has to bear high static and dynamic

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loads. For that purpose, additional flexibilizers and/or tougheners are to be added to the epoxy adhesive composition.

5 Structural epoxy adhesives have been described in several patent applications:

EP-A-0 197 892 describes a structural adhesive comprising an epoxy resin, a nitrogen comprising toughener and an accelerator. The problem described by this application is to provide a structural adhesive having a good storage
10 stability and a high curing rate.

EP-A-0 308 664 describes an epoxy adhesive composition comprising a butadiene-acrylonitrile copolymer in combination with a polyphenol-terminated polyurethane or polyurea.

15 EP-A-0 353 190 describes an epoxy adhesive composition comprising a butadiene-acrylonitrile copolymer in combination with a polyether-, polyester, polythioester or polyamid prepolymer terminated with a functionalized carbocyclic aromatic or araliphatic residue.

20 The technology according to EP-A-0 308 664 and EP-A-0 353 190 is called Mühlhaupt-technology. The problem described by both EP-A-0 308 664 and EP-A-0 353 190 is to improve the impact peel strength of the cured product. At low temperatures however, the impact peel strength is low.

25 WO 00/20483 relates to a composition comprising an epoxide-reactive copolymer having a glass-transition-temperature of -30°C or less, and a reaction product of a carboxylic acid anhydride with a di- or polyamine and a polyphenol or aminophenol.

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The cured product of WO 00/20483 has an impact peel strength of less than 20 N/mm at -40°C .

Since vehicles are normally exposed to varying climatic conditions, the cured product of a structural adhesive is required to have good mechanical properties at room temperature as well as at low temperatures. Because of their low impact peel strength values at low temperatures, the above known epoxy adhesives do not fully meet this requirement. Vehicles, parts of which are assembled by the above known epoxy adhesives, do consequently not fully comply with safety requirements, for example in a crash test.

A further disadvantage of the above known epoxy adhesive compositions is their relatively low impact behaviour on high strength metals both at moderate and at extreme temperatures. Due to this disadvantage, the use of the known epoxy adhesive compositions for assembling the parts of a high strength metal construction is limited.

It is an object of the present invention to provide an epoxy adhesive composition which upon curing results in a product having superior mechanical properties, in particular a high impact peel strength, at temperatures as low as -40°C , while maintaining the desirable mechanical properties of conventional epoxy adhesive compositions at room temperature.

It is a further object of the present invention to provide an epoxy adhesive composition which upon curing results in a product having a high impact peel strength on high strength metals.

According to the present invention, these problems are

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solved by a composition according to claim 1 comprising

a) a first epoxy resin,

b) a second epoxy resin modified with an acrylonitrile-butadiene rubber, the latter comprising
5 on average less than 25 wt% acrylonitrile, and

c) a toughener,

the total amount of component b) and component c) being
more than 30 % based on the total weight of the
composition, and the weight ratio of component c) to
10 component b) being greater than 1:1.

Preferred embodiments of the composition are defined in
the dependent claims.

The epoxy adhesive composition of the present invention
results upon curing in a product having an impact peel
15 strength of more than 35 N/mm at room temperature and of
more than 25 N/mm at -40°C. The vastly improved impact
strength at low temperatures allows the epoxy adhesive
composition to be used as a structural adhesive which upon
curing has a high crash resistance at any temperature of
20 use and satisfies the most stringent safety requirements.

Due to its improved toughening, the cured product of the
epoxy adhesive composition of the present invention has a
superior impact peel strength on high strength metals.
Assembly of high strength metal parts by the epoxy
25 adhesive composition of the present invention allows the
resulting high strength metal construction to be higher
loaded than a construction bonded with conventional
adhesives. The applicability of the epoxy adhesive
compositions of the present invention for the assembly of

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high strength metal parts is highly desirable, since bonding of high strength metal by welding is often not feasible.

5 Apart from the improved dynamic strength, the cured epoxy adhesive composition has an excellent static strength in a temperature range of from -40°C to $+80^{\circ}\text{C}$. The lap shear strength is higher than 25 MPa and the tensile strength is higher than 30 MPa. It has a young modulus of about 1500 MPa and a tensile elongation at break of more than 10%.

10 The epoxy adhesive composition of the present invention shows an excellent adhesion on coated steels like hot-dipped, electro-galvanized and bonazinc steel, pretreated aluminum, magnesium and composites.

15 After long-term artificial aging tests known to a skilled person, such as VDA, KKT, P1210 and 3C, or short term artificial aging tests (cataplasma), the strength values of the epoxy adhesive composition of the present invention are decreased by only 20 to 30%.

20 The first epoxy resin (component a) of claim 1 can be any kind of epoxy resin, such as DER 330 (low viscosity, undiluted, bisphenol A liquid epoxy resin), DER 331 (standard, undiluted, bisphenol A liquid epoxy resin) or DER 671 (low molecular weight solid epoxy resin), all of The Dow Chemical Company. Preferred examples of the first
25 epoxy resin are polyglycidyl ether of bisphenols, such as 2,2-bis-(4-hydroxyphenyl)-propane or bis-(4-hydroxyphenyl)-methane, of novolaks, which are formed by the reaction of formaldehyde with a phenol, and adducts of bisphenol A with aliphatic diols having glycidyl groups.

30 In a preferred embodiment, component a) is a mixture of at

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least two different epoxy resins. It is preferred that at least one epoxy resin is liquid at room temperature.

The second epoxy resin is modified with an acrylonitrile-butadiene rubber (component b). Preferably, component b) comprises at least 30 wt%, preferably at least 40 wt% of acrylonitrile-butadiene rubber. The acrylonitrile-butadiene rubber is preferably X8, X31 or any mixture of X8, X31 and X13 (wherein X stands for a copolymer rubber of the CTBN (carboxy-terminated butadiene-rubber) type and the term "mixture" means a "mixture of two or three of the components").

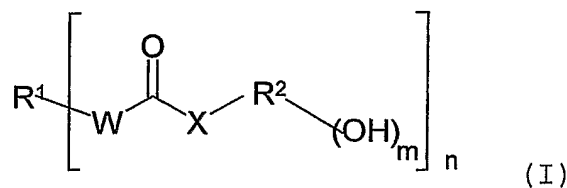
X8 is a CTBN type acrylonitrile-butadiene-rubber containing 17% acrylonitrile.

X13 is a CTBN type acrylonitrile-butadiene-rubber containing 26% acrylonitrile.

X31 is a CTBN type acrylonitrile-butadiene-rubber containing 10% acrylonitrile.

It is preferred that the epoxy adhesive composition comprises less than 20%, preferably less than 15% of acrylonitrile based on the total weight of the acrylonitrile-butadiene rubber.

The composition preferably comprises as toughener (component c) a compound of formula I

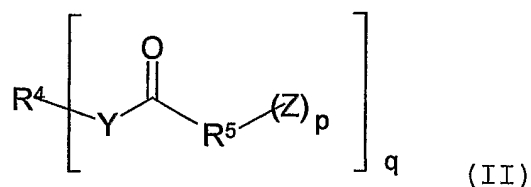


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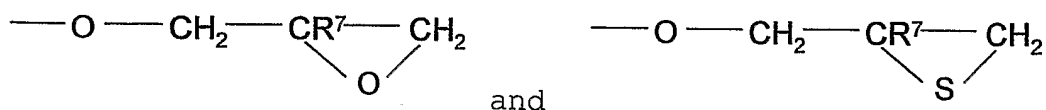
wherein m is 1 or 2, n is 2 to 6, R¹ is an n-valent radical of an elastomeric prepolymer after the removal of the terminal isocyanate, amino or hydroxyl group, the elastomeric prepolymer being soluble or dispersible in epoxy resin, W and X are independently -O- or -NR³-, at least one of W and X being -NR³-, R² is an m+1-valent radical of a polyphenol or aminophenol after the removal of the phenolic hydroxyl group and optionally of the amino group, and R³ is hydrogen, a C₁ to C₆ alkyl or phenol.

10 A detailed description of the toughener of formula I is given in EP-A-0 308 664 (page 5, line 14, to page 13, line 24), the disclosure of which is incorporated herein by reference.

In a further preferred embodiment, the composition comprises as component c) a compound of formula II



wherein p is 1 or 2, q is 2 to 6, Y is -O-, -S- or -NR⁶-, z is a radical selected from the group consisting of -OH, -NHR⁶, -OCN,



R⁴ is a residue of a hydroxyl-, mercapto- or amino-terminated polyether prepolymer or of a hydroxyl-,

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mercapto- or amino-terminated prepolymeric, segmented polyester, polythioester or polyamid, R⁵ is a carbocyclic aromatic or araliphatic p+1-valent radical with groups Z bonded directly to the aromatic ring, R⁶ is hydrogen, C₁ to 5 C₆ alkyl or phenyl, and R⁷ is methyl or hydrogen.

A detailed description of the toughener of formula II is given in EP-A-0 353 190 (page 3, line 51, to page 6, line 62), the disclosure of which is incorporated herein by reference.

10 The composition can comprise a mixture of both a compound of formula I and formula II as component c).

Examples of component c) are RAM A, RAM B or RAM C. RAM A, RAM B and RAM C are compounds of formula I, RAM A being allylphenol-terminated, RAM B being bisphenol A-terminated and RAM C being alkylphenol-terminated. A further example 15 is RAM 965 which is known to a skilled person.

A particular good impact behaviour at low temperature and on high strength steel is achieved if component b) is in an amount of from 14 to 20 % and component c) is in an amount of from 18 to 28 % based on the total weight of the 20 composition.

Particularly good results are achieved if the epoxy adhesive composition comprises a total amount of component b) and component c) of at least 35 wt%, preferably 38 wt%.

25 In a further preferred embodiment, the weight ratio of component c) to component b) is greater than 1.3:1, preferably greater than 1.5:1.

The epoxy adhesive composition according to the present invention can further include additives, such as fillers

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and accelerators, which are known to a person skilled in the art.

In a preferred embodiment, the composition comprises as an accelerator a solid solution of a nitrogen base having a boiling point above 130°C and a phenolic polymer which is an addition polymer of a phenol having an unsaturated substituent. (The term "solid solution" means the combination of the components in a solid one-phase system). A detailed description of such an accelerator is given in EP-A-0 197 892 (page 7, line 7, to page 10, line 28), the disclosure of which is incorporated herein by reference. Among these accelerators, EP 796 which is known to a skilled person is particularly preferred.

The epoxy adhesive composition is preferably used for the assembly of parts of a vehicle, such as cars, vans, lorries, trucks and trains. It can also be used for assembling parts of boats and aircrafts.

The epoxy adhesive composition of the present invention is preferably applied at a temperature of 40° to 65°C. It can be applied manually or automatically by a robot as normal beads, by swirling or by jet-streaming. The curing is starting at temperatures above 140°C.

EXAMPLES

25 Preparation of epoxy adhesive composition

7 wt% Struktol 3604 (Schill&Seilacher), 7 wt% Struktol 3914, 11 wt% DER 330, 20.2 wt% DER 331, 16.3 wt% DER 671, 24 wt% toughener RAM B and 0.2 wt% DW 0135 blue (Huntsman) are mixed in a laboratory planetary mixer at 90°C for 30

- 10 -

minutes. Then, 0.6 wt % adhesion promoter, such as an epoxy silane, 4.3 wt% fumed silica (Aerosil; Degussa) and 0.2 wt% of a wetting agent are added and the mixture is stirred at room temperature for another 30 minutes. Then,
5 4.2 wt% DICY (Cyanoguanidine, Airproducts), 0.75 wt% of accelerator EP 796 (Huntsman) and 3.2 wt% of a gelling compound are added and the mixture is stirred at room temperature for another 15 minutes. All mixing steps are performed under vacuum.

10 Testing of epoxy adhesive composition

The adhesive itself is showing the following standard values after curing at temperatures higher than 140°C.

E modulus: about 1500 MPa

Tensile strength: about 35 MPa

15 Elongation: about 15 %

Viscosity at 45°C: 158 Pas

Yield point at 45°C: 47 Pa

Lap shear (1.5 mm; CRS 1403): > 25 MPa

Impact peel strength at room temperature (1 mm; CRS 1403):
20 > 35 N/mm

Impact peel strength at -40°C (1 mm; CRS 1403): > 25 N/mm

VDA testings were performed on pretreated aluminum, hot dipped, electro galvanised and bonazinc coated steel and showed a decrease in strength by only 20 to 30%. Other
25 artificial aging tests like KKT, P 1210, 3C and cataplasma showed similar results.

TABLE 1

Low temperature impact behaviour:

Sample	Impact peel strength at room temperature [N/mm]	Impact peel strength at -40°C [N/mm]	Component b/ amount wt%	Component c/ amount wt%	Ratio of component c to component b
BM 1496C 2	53	43	Struktol 3914/ 20	RAM 965 / 30	3:2
C 13	40	39	Struktol 3914/20	RAM B/ 30	3:2
C 14	32	29	Struktol 3914/ 15	RAM B/ 25	1.7:1
C 16	47	41	Struktol 3914/ 14	RAM B/ 28	2:1
C 18	37	40	Struktol 3914/ 12	RAM B/ 24	2:1
C 27	54	47	Struktol 3604/ 14	RAM B/ 28	2:1
C 29	51	30	Struktol 3914/ 14	RAM B/ 20	1.4:1
C30 (comparative)	30	12	Struktol 3914/ 15	RAM B/ 15	1:1

C 32	54	41	Struktol 3604 and 3914/7,7	RAM B/ 24	1.7:1
C 39	42	47	Struktol 3604 and 3914/7,7	RAM 965/ 24	1.7:1
C 34 (com- parative)	42	19	Struktol 3614/ 14	RAM B/ 24	1.7:1
C 36	43	45	Struktol 3914-1/ 14	RAM B/ 24	1.7:1
C 37	44	44	Struktol 3614-2/ 14	RAM B/ 24	1.7:1
compara- tive struct. adhesive acc. to Mühlhaupt- technology	44	10	Struktol 3604/ 14	RAM 965/ 14	1:1
compara- tive struct. adhesive acc. to Mühlhaupt- technology	38	13	Struktol 3614/ 14	RAM 965/ 14	1:1

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In Table 1, the rubber modified epoxy resins (component b) are characterized as follows:

Struktol 3604 is a rubber modified epoxy resin consisting of 60% diglycidyl ether of bisphenol A (DGEBA) and 40% X8.

- 5 Struktol 3614 is a rubber modified epoxy resin consisting of 60% DGEBA and 40% X13.

Struktol 3914 is a rubber modified epoxy resin consisting of 60% DGEBA and 40% of a mixture of X31 and X8, wherein X31:X8 = 1:1.

- 10 Struktol 3914-1 is a rubber modified epoxy resin consisting of 60% DGEBA and 40% of a mixture of X31 and X8, wherein X31:X8 = 3:1.

- Struktol 3914-2 is a rubber modified epoxy resin consisting of 60% DGEBA and 40% of a mixture of X31 and
15 X8, wherein X31:X8 = 1:3.

The values of the impact peel strength were determined according to ISO 113 43.

- As can be seen from Table 1, the epoxy adhesive compositions according to the present invention have a
20 significantly higher impact peel strength at -40°C than the conventional epoxy adhesive compositions.

TABLE 2

Impact peel strength on high strength steels: values in N/mm at room temperature

Steel type	BM 1496C32 (according to invention)	BM 1480 (comparative)	BM 1496V (comparative)	BM 1040 (comparative)
H300XD Z100, 1mm	43	36	33	15
H400TD Z100, 1mm	42	34	31	14
RAGAL600DP Z100, 1mm	31	29	21	8
DOCOL 1000DP ZE75/75, 0.9mm	33	21	22	6

5

H300XD Z100, H400TD Z100, RAGAL600DP Z100, DOCOL 1000DP ZE75/75 are high strength steels known to a skilled person. As can be seen from Table 2, the epoxy adhesive composition according to the present invention shows a significantly higher impact peel strength on high strength steel compared to known structural adhesive compositions.

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TABLE 3

Lap shear strength on high strength steel: values in MPa
at room temperature

Steel type	BM 1496C32 (according to invention)	BM 1480 (compara- tive)	BM 1496V (compara- tive)	BM 1040 (compara- tive)
H300XD Z100, 1mm	32	33	34	39
H400TD Z100, 1mm	31	38	37	37
RAGAL600D P Z100, 1mm	34	35	35	35
DOCOL 1000DP ZE75/75, 0,9mm	33	37	38	37

5

Table 3 shows the lap shear strengths values of known structural adhesive compositions being maintained in the epoxy adhesive composition according to the present invention.

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Claims

1. An epoxy adhesive composition comprising

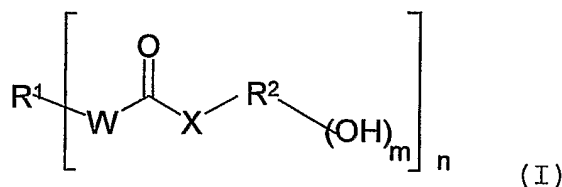
a) a first epoxy resin,

b) a second epoxy resin modified with an acrylonitrile-butadiene rubber, the latter comprising on average less than 25 wt% acrylonitrile, and

c) a toughener,

the total amount of component b) and component c) being more than 30 % based on the total weight of the composition, and the weight ratio of component c) to component b) being greater than 1:1.

2. A composition according to claim 1 comprising as component c) a compound of formula I



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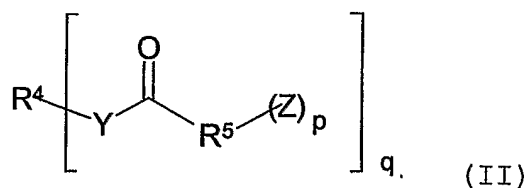
20

wherein m is 1 or 2, n is 2 to 6, R¹ is an n-valent radical of an elastomeric prepolymer after the removal of the terminal isocyanate, amino or hydroxyl group, the elastomeric prepolymer being soluble or dispersible in epoxy resin, W and X are independently -O- or -NR³-, at least one of W and X being -NR³-, R² is an m+1-valent radical of a polyphenol or aminophenol after the removal of the phenolic

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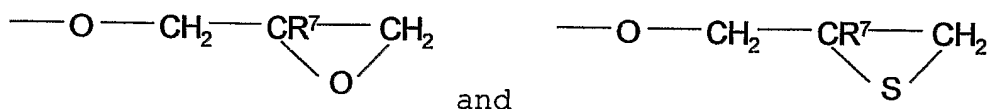
hydroxyl group and optionally of the amino group, and R^3 is hydrogen, a C_1 to C_6 alkyl or phenol.

3. A composition according to claim 1 or claim 2 comprising as component c) a compound of formula II



5

wherein p is 1 or 2, q is 2 to 6, Y is $-O-$, $-S-$ or $-NR^6-$, Z is a radical selected from the group consisting of $-OH$, $-NHR^6$, $-OCN$,



10

R^4 is a residue of a hydroxyl-, mercapto- or amino-terminated polyether prepolymer or of a hydroxyl-, mercapto- or amino-terminated prepolymeric, segmented polyester, polythioester or polyamid, R^5 is a carbocyclic aromatic or araliphatic $p+1$ -valent radical with groups Z bonded directly to the aromatic ring, R^6 is hydrogen, C_1 to C_6 alkyl or phenyl, and R^7 is methyl or hydrogen.

15

4. A composition according to one of the preceding claims, component b) comprising at least 30 wt%, preferably at least 40 wt% of acrylonitrile-butadiene rubber.

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5. A composition according to one of the preceding claims, component b) comprising a mixture of three different acrylonitrile-butadiene rubbers:
 - b1) comprising about 10 wt% of acrylonitrile,
 - 5 b2) comprising about 17 wt% of acrylonitrile, and
 - b3) comprising about 26 wt% of acrylonitrile.
6. A composition according to one of the preceding claims comprising component b) in an amount of from 14 to 20 % and component c) in an amount of from 18
10 to 28 % based on the total weight of the composition.
7. A composition according to one of the preceding claims, the acrylonitrile-butadiene rubber of component b) comprising less than 20 wt%, preferably less than 15 wt% of acrylonitrile.
- 15 8. A composition according to one of the preceding claims comprising a total amount of component b) and component c) of at least 35 wt%, preferably of at least 38 wt%.
9. A composition according to one of the preceding
20 claims wherein the weight ratio of component c) to component b) is greater than 1.3:1, preferably greater than 1.5:1.
10. A composition according to one of the preceding
25 claims, component a) being a mixture of at least two different epoxy resins.
11. A composition according to one of the preceding claims, component a) comprising at least one epoxy resin that is liquid at room temperature.

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12. A composition according to one of the preceding claims, comprising EP 796 as accelerator.
13. Use of the epoxy adhesive composition according to one of the preceding claims for the assembly of parts
5 of a vehicle.
14. A vehicle, parts of which are assembled by the epoxy adhesive composition according to one of claims 1 to 12.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP2005/002361

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08G59/18 C09J163/00 C08G59/42 C08L63/00

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B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
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Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2003/187154 A1 (SCHOENFELD RAINER ET AL) 2 October 2003 (2003-10-02) the whole document -----	1-14
A	EP 0 308 664 A (CIBA-GEIGY AG) 29 March 1989 (1989-03-29) the whole document -----	1-14
A	EP 0 353 190 A (CIBA-GEIGY AG) 31 January 1990 (1990-01-31) the whole document -----	1-14

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

Information on patent family members

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