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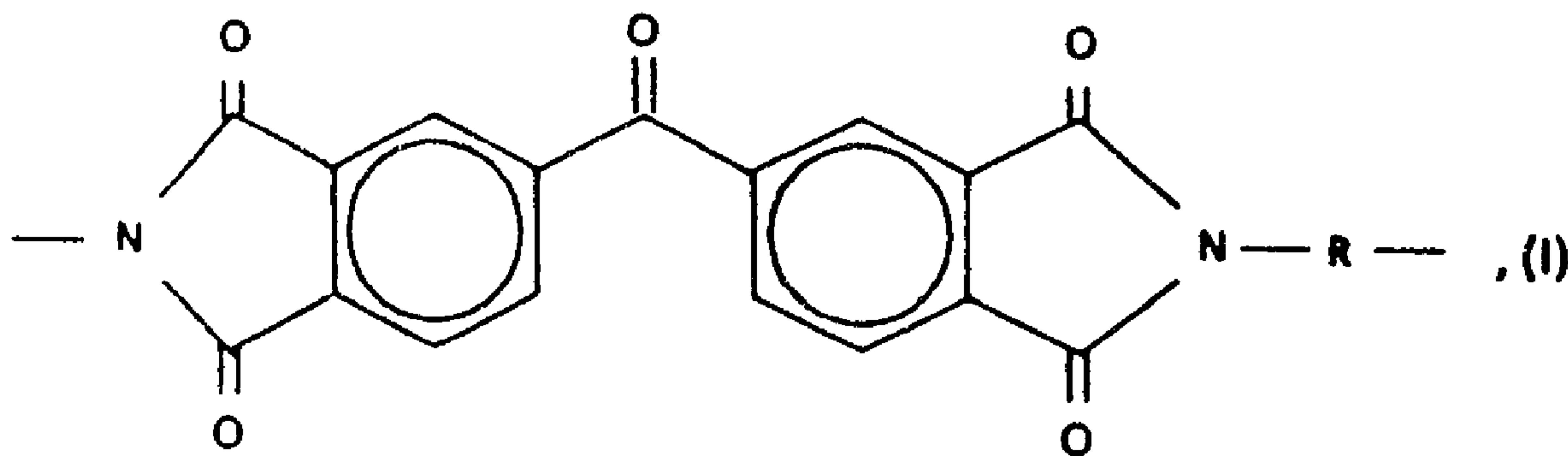
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(54) Titre : PARTICULES COMPOSITES FORMEES D'UNITES STRUCTURALES DE POLYIMIDE ET A NOYAU DE
REMPLISSAGE

(54) Title: A COMPOSITE PARTICLE COMPRISING POLYIMIDE STRUCTURAL UNITS AND A CORE MADE OF A
FILLER



(57) Abrégé/Abstract:

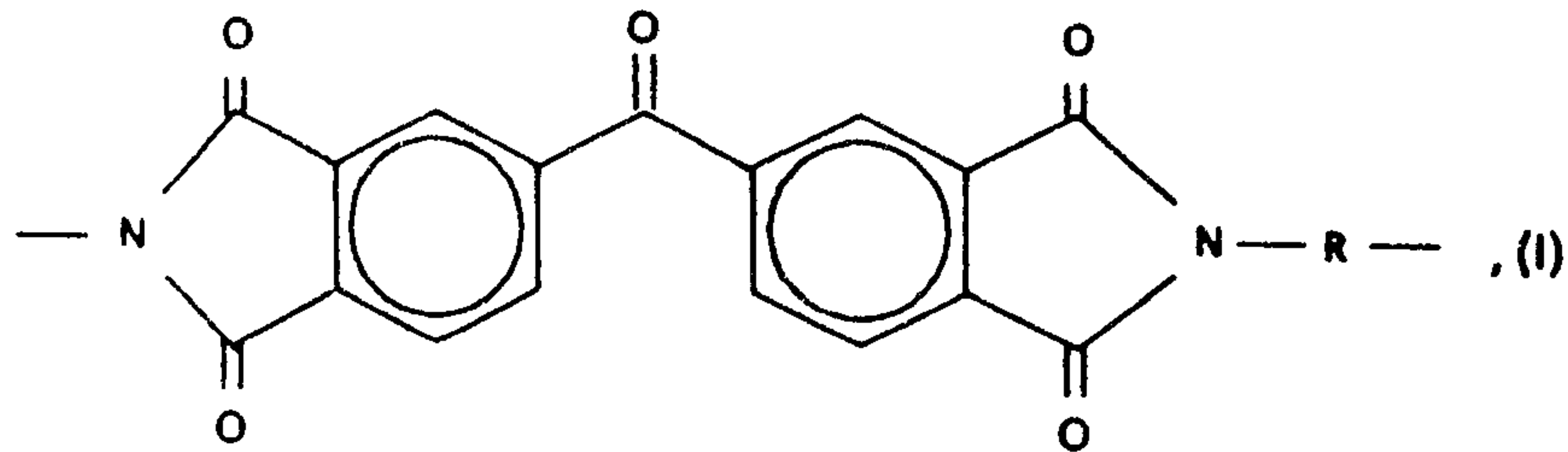
There are disclosed composite particles formed of polyimide structural units of the general formula (see formula I) wherein R represents 2,4- and/or 2,6-toluene or a biphenylmethelyene group and of filler cores. They may be compressed to shaped articles, Glass, mica, graphite or PTFE may be used as fillers.



ABSTRACT OF THE DISCLOSURE:

There are disclosed composite particles formed of polyimide structural units of the general formula

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wherein R represents 2,4- and/or 2,6-toluene or a biphenylmethelyene group and of filler cores. They may be compressed to shaped articles. Glass, mica, graphite
15 or PTFE may be used as fillers.

The invention relates to composite particles comprising polyimide structural units and a filler core, a process for producing the same as well as a shaped article made of such composite particles.

5 It is known to use powder mixtures of polyimides and non-metallic fillers for the production of shaped articles. To this end, polyimide powder and a powdery filler are intimately mixed and sintered under shaping. However, the shaped articles obtained in this manner all
10 have poorer mechanical properties than shaped articles exclusively consisting of polyimide.

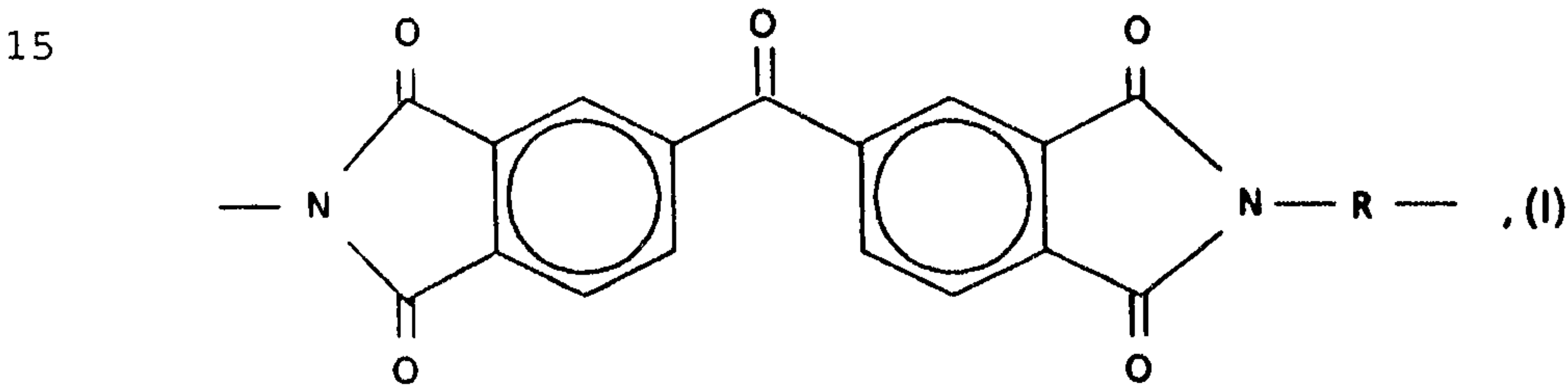
 In GB-A - 2,176,193 the production of polyimide particles including a filler core is described. The filler is dispersed in a liquid medium in the
15 disintegrated state and introduced at any stage before the polyimide production. Thus, the polyimide is being produced in the presence of the filler. This is achieved by initially reacting an aromatic tetracarboxylic acid dianhydride with an aromatic diamine to polyamidic acid
20 in a polar solvent. However, the filler dispersed in the liquid medium is added to the reaction mixture prior to carrying out imidation to the polyimide. In the course of imidation, the polyimide deposits on the surface of the filler particles, the latter thus getting
25 coated entirely or partly.

 A disadvantage of this process consists in the comprehensive reaction control via the polyamidic acid.

This course also calls for subsequent condensation because imidation frequently is not completely successful. Also, it is not possible to produce polyimide particles having defined grain sizes, the
5 pourability, thus, being unsatisfactory. Moreover, the end product does not have a high bulk density.

It is the object of the invention to produce composite particles of the initially defined kind, that do not have such disadvantages.

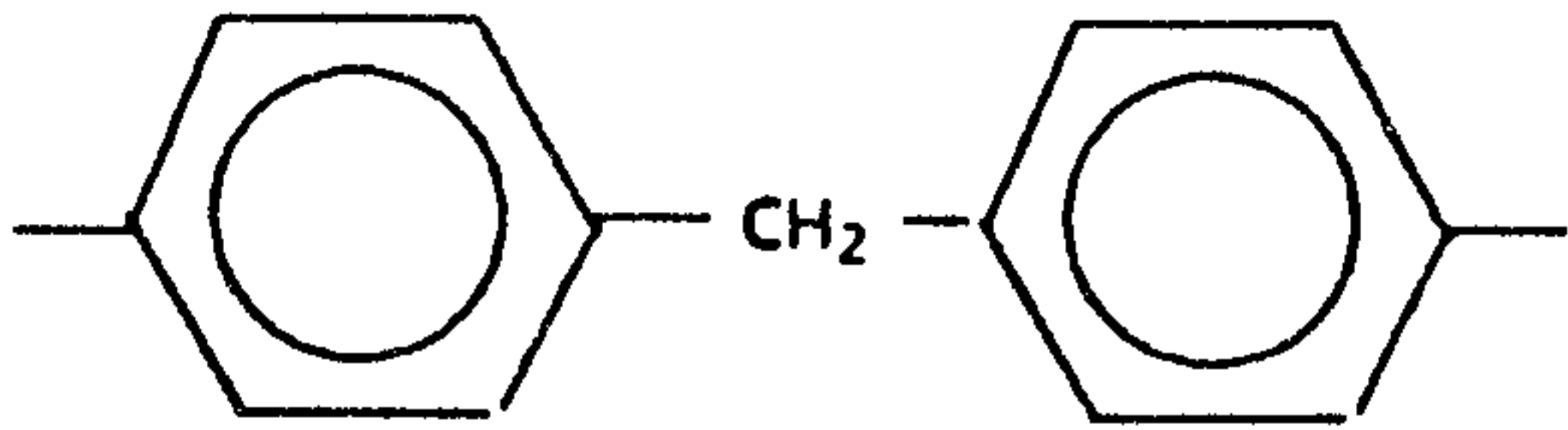
10 The composite particles according to the invention comprise polyimide structural units of the general formula



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wherein R represent 2,4- and/or 2,6-toluene or a group of the formula

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By using these polyimide structural units, the process control via the polyamidic acid is obviated. The composite particles according to the invention are producible in a simple manner by precipitating the polyimide from a solution in the presence of filler particles. In doing so, composite particles of defined grain sizes exhibiting a good pourability and a high bulk density are formed.

Preferably, the composite particles according to the invention comprise between 1 and 50 % by mass of polyimide.

The filler may be comprised, i.a., of graphite, glass, MoS_2 , mica or, preferably, polytetrafluoroethylene (PTFE). The advantages of the composite particles according to the invention are particularly apparent if PTFE is used as the filler. It is known that, e.g., the sensitivity of PTFE powder to shearing makes it difficult to process, that its tendency to agglomerating allows its transport over large distances only under cooling of the containers, and that also its pourability is poor. These difficulties may be eliminated, if the PTFE powder at least partially is coated with a polyimide of the structural units indicated above. It will already do if the composite particle is comprised of polyimide by less than 20 % by mass, i.e., if the PTFE powder is coated only by a thin polyimide layer.

A preferred embodiment of the composite particles according to the invention consists in that the particles have a maximum diameter of 3 mm and their bulk density amounts to between 0.20 and 0.70 g/cm³,
5 preferably between 0.30 and 0.40 g/cm³. Such high bulk densities facilitate the compression and sintering of the composite particles, because shaping need not be started with large molds and a precise filling following the contours of the mold is safeguarded.

10 The composite particles according to the invention are very well suited for the production of shaped articles by compression at pressures preferably of between 200 and 800 bar and at temperatures of between 20 and 400°C.

15 The shaped articles according to the invention altogether exhibit better mechanical, in particular better tribological, properties than those obtained with presently known composite particles. Composite particles having cores of PTFE, for instance, may be used to
20 produce bearings or tuyeres exposed to thermal stresses, which, in addition, will stand out for an improved hardness as compared to PTFE and, thus, for an improved abrasive strength.

The invention also relates to a process for
25 producing such composite particles, which is characterized in that filler particles are dispersed in a solution of the polyimide and the dispersion obtained

is introduced into an aqueous precipitant, the filler particles being coated by a polyimide layer at least partially, whereupon the products obtained are separated, washed with water, dried and, if desired,
5 disintegrated.

In the process according to the invention, a solution of the polyimide in an aprotic polar solvent, such as dimethylformamide, dimethylacetamide, dimethylsulfoxide or N-methylpyrrolidone, containing 1
10 to 30 % by mass of polyimide, is best used. The preparation of such a solution is described, for instance, in US-A- 3,708,458.

The grain size of the filler may vary within wide ranges. With the process of the invention, a fibrous
15 filler having staple lengths up to 3 mm may also be employed.

The dispersion can be prepared in a simple manner by stirring the filler into the polyimide solution till homogeneity.

20 To precipitate the polyimide, the dispersion is introduced into an aqueous precipitant, preferably a water/DMF mixture, for instance, by applying the method described in AT-B-387,227. Subsequently, the precipitated product is separated, dried and, if
25 desired, disintegrated. Disintegration may be effected, for instance, by means of an impact mill. The composite particles forming during grinding have a closed or

partially closed polyimide coating.

A substantial advantage of the process according to the invention consists in that the viscosity of the polyimide solution is no limiting parameter. Therefore,
5 it is possible to introduce a multiple of the polyimide content of filler, thus, producing composite particles comprising extremely thin polyimide layers.

It is also possible to work up filler mixtures, such as graphite and carbon fibers. According to the
10 process of the invention, the formation of clusters is excluded, anyway. The pourability of the composite particles according to the invention, in particular those having cores containing PTFE, is preserved even at elevated temperatures (up to 300°C) as in contrast to
15 the mixtures known today. Thus, handling during processing is considerably facilitated, in particular, during possibly necessary predrying.

The invention will be described in more detail by way of the following examples, in which the polyimide
20 used comprised structural units of formula (I), R representing about 80 % by mol of 2,4- and/or 2,6-toluene and about 20 % by mol of the biphenylmethylene group.

Example 1:

25 The polyimide was taken up in DMF to prepare a solution of 25 % by mass. Into this solution, 15 % by mass (based on the polyimide) graphite having a particle

size of $<6 \mu\text{m}$ were stirred. After this, the dispersion obtained was introduced into a water/DMF mixture (2:1) and the precipitated product was washed free of solvent. Drying was effected by means of hot air. The grains
 5 obtained were ground to a grain size of 10 to $150 \mu\text{m}$ in an impact mill. The bulk density of the composite particles obtained was 0.45 g/cm^3 . They consisted of polyimide by 85 %.

Subsequently, the composite particles were
 10 compressed to a shaped article at a temperature of 350°C and a pressure of 350 bar.

The shaped article had a smooth uniform surface and was readily machinable.

15	Tensile strength:	65 N/mm ²
	Tensile elongation:	1.8 %
	Bending strength:	105 N/mm ²
	Edge fiber elongation:	5 %

20 Example 2:

80 % by mass (based on the polyimide) PTFE micropowder (grain size $<10 \mu\text{m}$) was stirred into a solution containing 7 % by mass polyimide in DMF, the dispersion obtained was precipitated in a water/DMF
 25 mixture (2:1), and the precipitated product was washed free of solvent. Drying was effected by means of hot air.

The solid obtained consisted of 80 % by mass PTFE and 20 % by mass polyimide and was ground to a powder having a grain size of 20 to 100 μm in an impact mill under nitrogen cooling at $T = -30^{\circ}\text{C}$. After predrying at 5 320°C under vacuum, the powder was compressed at a temperature of 20°C and a pressure of 550 bar. After release from the mold, the shaped article was sintered in the forced-air oven at 370°C .

10 The finished shaped article had a homogenous brown coloring and a smooth surface free of pores. It was machinable very well.

Tensile strength: 20 N/mm²

Tensile elongation: 200 %

15

Example 3:

15 % by mass (based on the polyimide) graphite (particle size $< 6 \mu\text{m}$) was stirred into a solution of 15 % by mass polyimide in DMF, the dispersion was diluted 20 with DMF to a total content of 15 % solids and was precipitated in a water/DMF mixture (1:1).

Substantially finer solid particles were obtained than in Example 1 (the particle size being 1 to 2 mm at a flaky structure, bulk density 0.25 g/cm^3). They were 25 washed with hot water, dried with hot air and directly compressed to a shaped article under the conditions indicated in Example 1, without fine grinding.

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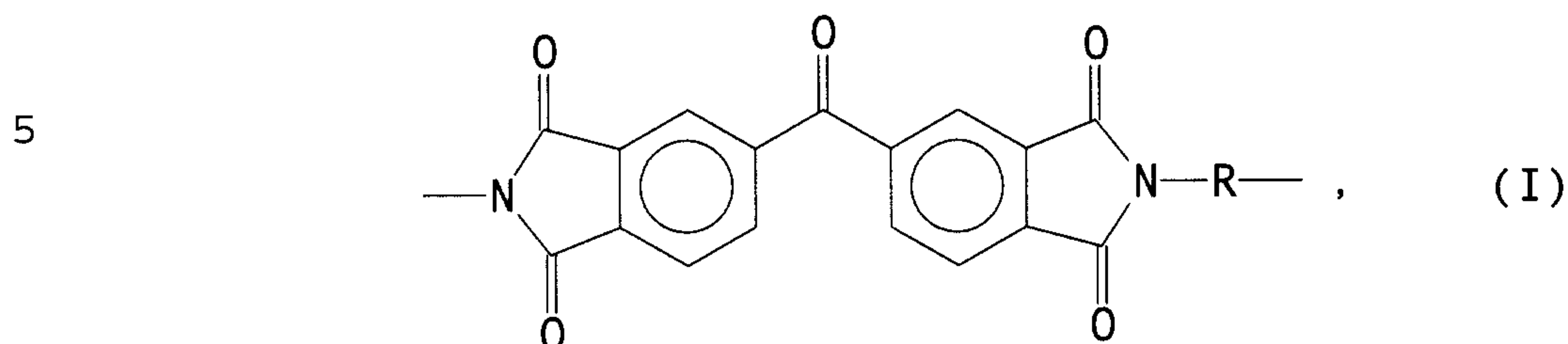
The shaped article had a smooth surface and was free of pores and inclusions.

	Tensile strength:	100 N/mm ²
5	Tensile elongation:	3.5 %
	Bending strength:	165 N/mm ²
	Edge fiber elongation:	5 %

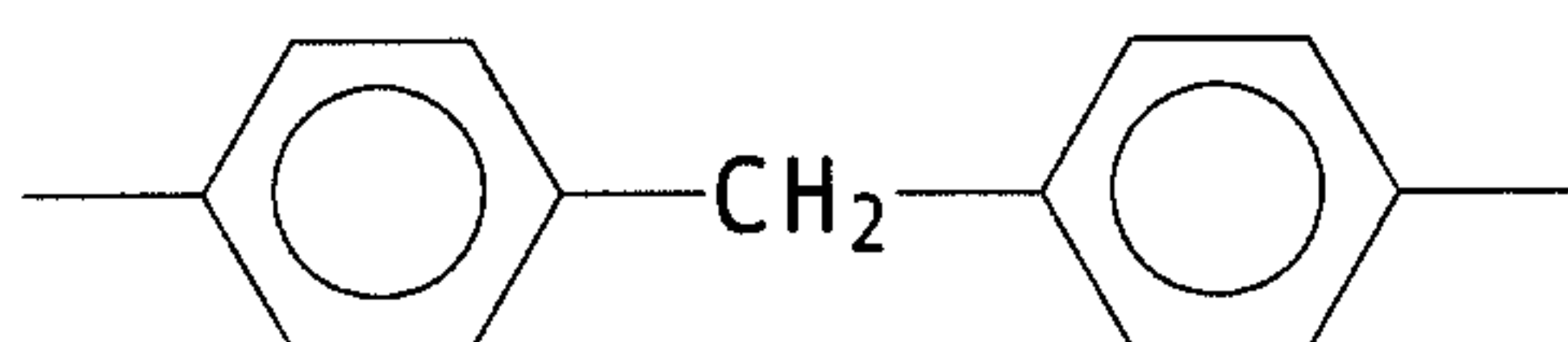
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CLAIMS:

1. A composite particle comprising polyimide structural units of the general formula



- wherein R represents at least one aromatic constituent from the group consisting of 2,4-toluene and 2,6-toluene or a
10 group of the formula



and a core made of a filler.

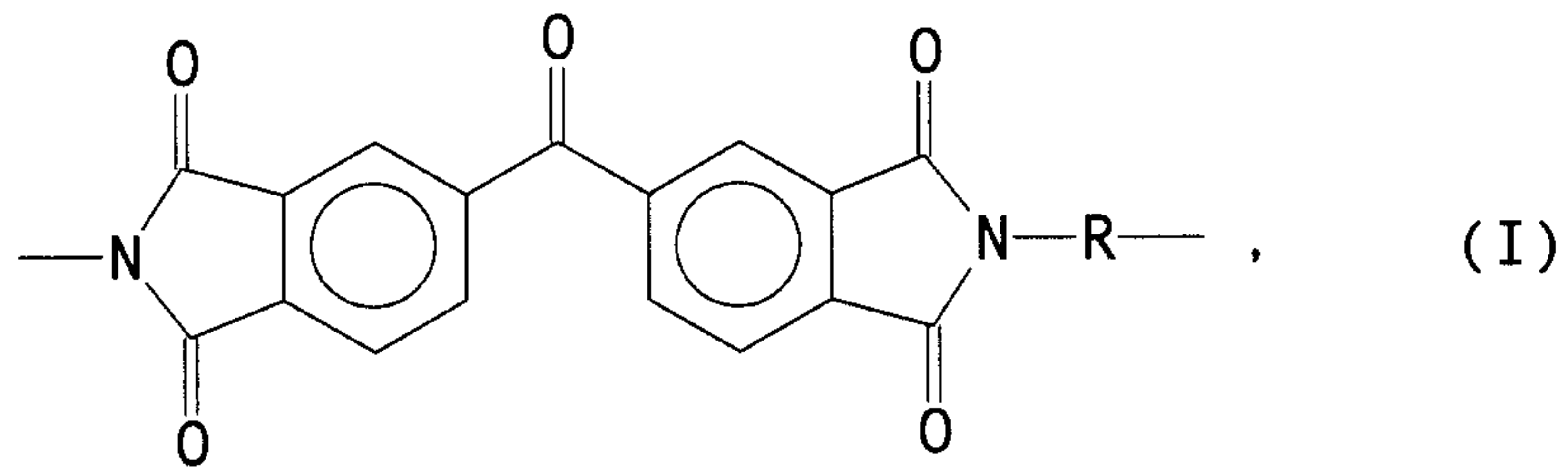
2. A composite particle as set forth in claim 1,
15 which comprises 1 to 50% by mass polyimide.
3. A composite particle as set forth in claim 1,
wherein said filler is selected from the group consisting of graphite, glass, MoS₂ and mica.
4. A composite particle as set forth in claim 1,
20 wherein said filler is comprised of polytetrafluoroethylene (PTFE).
5. A composite particle as set forth in claim 1,
wherein said particle has a maximum diameter of 3 mm and a bulk density ranging between 0.20 and 0.70 g/cm³.

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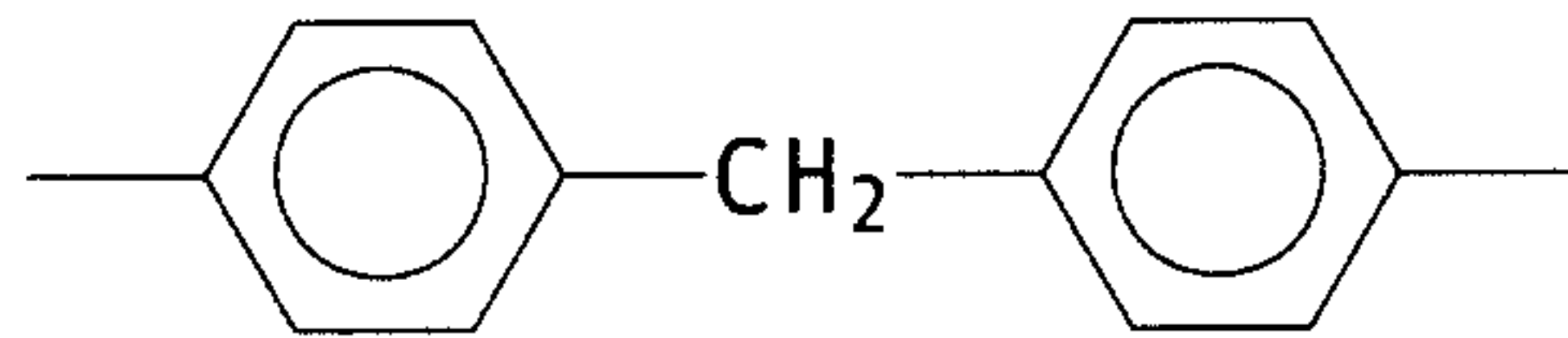
6. A composite particle as set forth in claim 5,
wherein said bulk density ranges between 0.30 and 0.40 g/cm³.

7. A process for producing a composite particle
including polyimide structural units of the general formula

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wherein R represents at least one aromatic constituent from
10 the group consisting of 2,4-toluene and 2,6-toluene or a
group of the formula



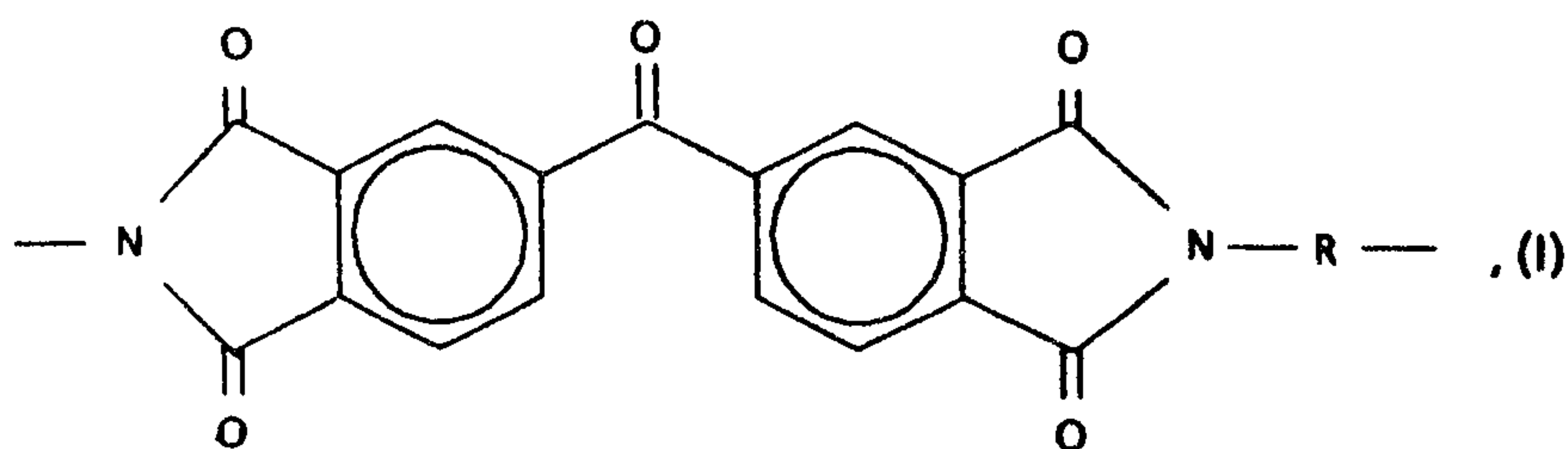
16 and a core made of a filler, which process comprises
 17 dispersing filler particles in a solution of said
 18 polyimide so as to obtain a dispersion,
 19 providing an aqueous precipitant and introducing said
 20 dispersion into said aqueous precipitant, thus causing
 21 said filler particles to be coated by a layer of said
 22 polyimide at least partially so as to obtain composite
 23 particle products,
 24 separating said products and washing and drying them.

1 8. A process as set forth in claim 7, wherein said
 2 products are disintegrated.

1 9. A process as set forth in claim 7, wherein a
 2 solution of said polyimide in an aprotic polar solvent
 3 containing 1 to 30 % by mass polyimide is used.

1 10. A process as set forth in claim 9, wherein said
 2 aprotic polar solvent is selected from the group
 3 consisting of dimethylformamide, dimethylacetamide,
 4 dimethylsulfoxide and N-methylpyrrolidone.

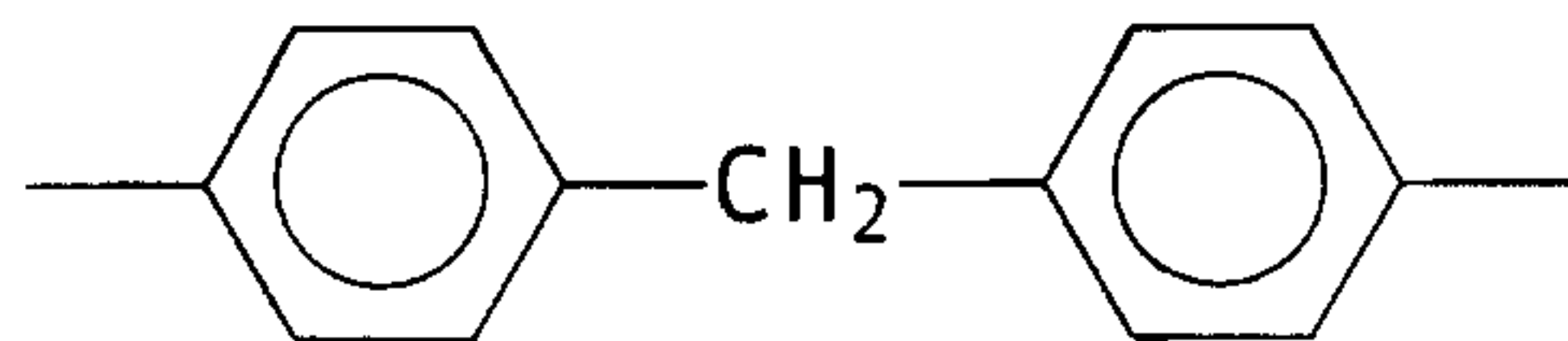
1 11. A shaped article comprised of composite
 2 particles including polyimide structural units of the
 3 general formula



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wherein R represents at least one aromatic constituent from the group consisting of 2,4-toluene and 2,6-toluene or a group of the formula

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and a core made of a filler, which shaped article is produced by compression of said composite particles at a pressure of between 200 and 800 bar and at a temperature of between 20 and 400°C.

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PATENT AGENTS

