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(54) TUYAU DE PLASTIQUE MULTICOUCHE
(54) MULTILAYER PLASTIC PIPE

(57) A plastic pipe having improved resistance to chemicals and improved mechanical properties is disclosed. The pipe comprises at least three layers: an outer layer, an intermediate layer made of a moulding compound based on a mixture of a polyamide and a polyglutarimide and an inner layer made of a moulding compound based on a polyvinylidene fluoride. The outer layer is preferably made of a moulding compound based on a polyamide. The pipe has an outstanding resistance to and a good barrier action with respect to diffusion of (petro) chemicals, solvents and fuels. Since the adjacent layers are adhesively bonded to one another, no delamination occurs on thermal expansion or flexing of the pipe. The pipe is preferably used in the motor vehicle sector, for carrying brake, cooling and hydraulic fluids and fuel.

Abstract:

A plastic pipe having improved resistance to chemicals and improved mechanical properties is disclosed. The pipe comprises at least three layers: an outer layer, an intermediate layer made of a moulding compound based on a mixture of a polyamide and a polyglutarimide and an inner layer made of a moulding compound based on a polyvinylidene fluoride. The outer layer is preferably made of a moulding compound based on a polyamide. The pipe has an outstanding resistance to and a good barrier action with respect to diffusion of (petro) chemicals, solvents and fuels. Since the adjacent layers are adhesively bonded to one another, no delamination occurs on thermal expansion or flexing of the pipe. The pipe is preferably used in the motor vehicle sector, for carrying brake, cooling and hydraulic fluids and fuel.

Multilayer plastic pipe

The invention relates to a multilayer plastic pipe.

Plastic pipes made from polyamide are known and are employed in a variety of applications. In order to achieve their objective, the pipes must, inter alia, be inert to the medium flowing in them, and resistant to high and low temperatures and mechanical stresses.

Single-layer pipes are not always capable of satisfying the necessary requirements. In the transport of, for example, aliphatic or aromatic solvents, motor fuels or the like, they exhibit considerable disadvantages, such as poor barrier action with respect to the medium, undesired changes in dimension or inadequate resistance to mechanical stresses.

Attempts have been made to overcome these disadvantages by means of multilayer pipes (DE-A 35 10 395, 37 15 251, 38 21 723, 40 01 125 and 40 01 126). However, practical implementation of these proposals has shown that, although some disadvantages can be overcome, the overall property profile is still unsatisfactory.

French Patent 2 602 515 describes a two-layer pipe having an outer layer of polyamide 11 and an inner layer of plasticized polyvinylidene fluoride. However, investigations have shown that the barrier action with respect to the medium flowing through the pipe is unsatisfactory.

In particular, the permeation of methanol-containing fuels could not be sufficiently reduced by the above proposals.

The reason why the reduction of permeation by use of novel intermediate layers is of critical importance is, in particular, the fact that the legally permitted emission values are constantly being reduced further.

An object of the invention was to develop a polyamide pipe having a good barrier action with respect to the transported medium, in particular to methanol-containing fuels, satisfactory dimensional stability, for example at high and low temperatures, and satisfactory resistance to mechanical stresses.

The invention provides a multilayer plastic pipe comprising at least:

I. an outer layer

II. an intermediate layer adjacent to the inner layer, which intermediate layer is made of a moulding compound based on a mixture of
  a. a polyamide, and
  b. a polyglutarimide

III. an inner layer made of a moulding compound based on a polyvinylidene fluoride,

wherein the adjacent layers are adhesively bonded to one another.

First choice for the outer layer according to I. and for the component II.a are aliphatic homo- and copolyamides. Examples are polyamides 4.6, 6.6, 6.12, 8.10, 10.10 or the like. Preference is given to polyamides 6, 10.12, 11, 12.12 and in particular 12. [The designation of the polyamides corresponds to the international standard, where the first number(s) indicates the number of carbon atoms in the starting diamine and the last number(s) indicates the number of carbon atoms in the dicarboxylic acid. If only one number is given, it indicates that the starting material was an α-ω-aminocarboxylic acid or the lactam derived therefrom (H. Domininghaus, Die Kunststoffe und ihre Eigenschaften [Plastics and their properties], page 272, VDI-Verlag (1976)).]

If copolyamides are used, they may contain, for example, adipic acid, sebacic acid, suberic acid, isophthalic acid or terephthalic acid as co-acid or bis(4-aminocyclohexyl)methane, trimethylhexamethylenediamine, hexamethylenediamine or the like as co-diamine.

The preparation of these polyamides is known (for example D. B. Jacobs, J. Zimmerman, Polymerization Processes, pp. 424-67, Interscience Publishers, New York (1977); DE-B 21 52 194).

Other suitable polyamides are mixed aliphatic/aromatic polycondensates as are described, for example, in US Patents 2,071,250, 2,071,251, 2,130,523, 2,130,948, 2,241,322, 2,312,966, 2,512,606 and 3,393,210, and in Kirk-Othmer, Encyclopedia of Chemical Technology, 3rd edition, vol. 18, Wiley & Sons (1982), pp. 328 and 435. Other polycondensates which are suitable as polyamides are poly(ether ester amides) and poly(ether amides). Such products are described, for example, in DE-A 27 12 987, 25 23 991 and 30 06 961.

The molecular weight (number average) of the polyamides is greater than 5,000, preferably greater than 10,000, corresponding to a relative viscosity (η_{rel}) in the range from 1.65 to 2.4.

As polyamides for the components according to I. and II.a., identical or different types of polyamide may be selected.

Preference is given to polyamides which contain ≤ 50% of amino end groups, in particular < 20% of amino end groups.

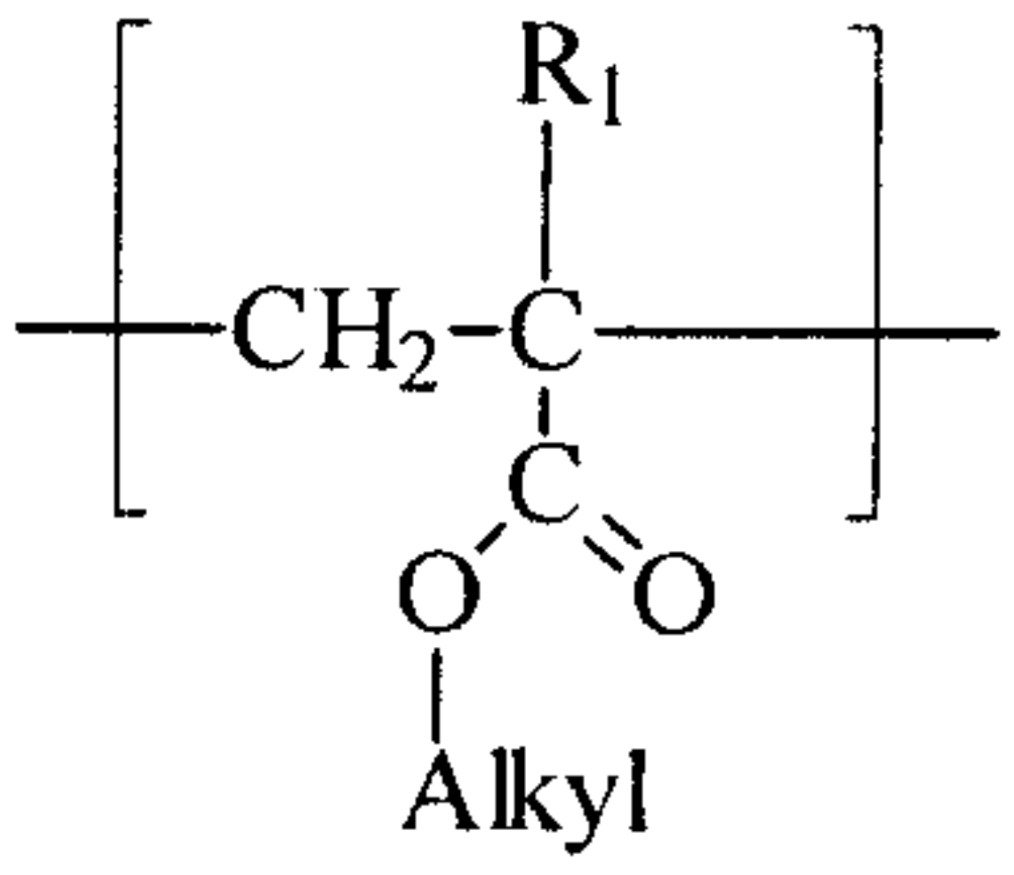
The polyamides of the outer layer according to I. and the component II.a. can contain up to 40% by weight of other thermoplastics, provided that these do not adversely affect the properties according to the invention. Particular mention may here be made of polycarbonate [H. Schnell, Chemistry and Physics of Polycarbonates, Interscience Publishers, New York (1981)], acrylonitrile/styrene/byutadiene copolymers (Houben-Weyl, Methoden der organischen Chemie [Methods of Organic Chemistry], vol. 14/1, Georg Thieme Verlag, Stuttgart, pp. 393-406; Ullmans Encylopädie der technischen Chemie [Ullman's Encyclopedia of Industrial Chemistry], 4th edition, vol. 19, Verlag Chemie, Weinheim (1981), pp. 279-284), acrylonitrile/styrene/acrylate copolymers (Ullmanns Encyclopadie der technischen Chemie [Ullman's Encyclopedia of Industrial Chemistry], 4th edition, vol. 19, Verlag Chemie, Weinheim (1981), pp. 277-295), acrylonitrile/styrene copolymers (Ullmann's Encylopadie der technischen Chemie [Ullmann's Encyclopdedia of Industrial

Chemistry] 4th edition, vol. 19, Verlag Chemie Weinheim (1981), pp. 273 ff.) or polyphenylene ethers (DE-A 32 24 691 and 32 24 692, and US Patents 3,306,874, 3,306,875 and 4,028,341.

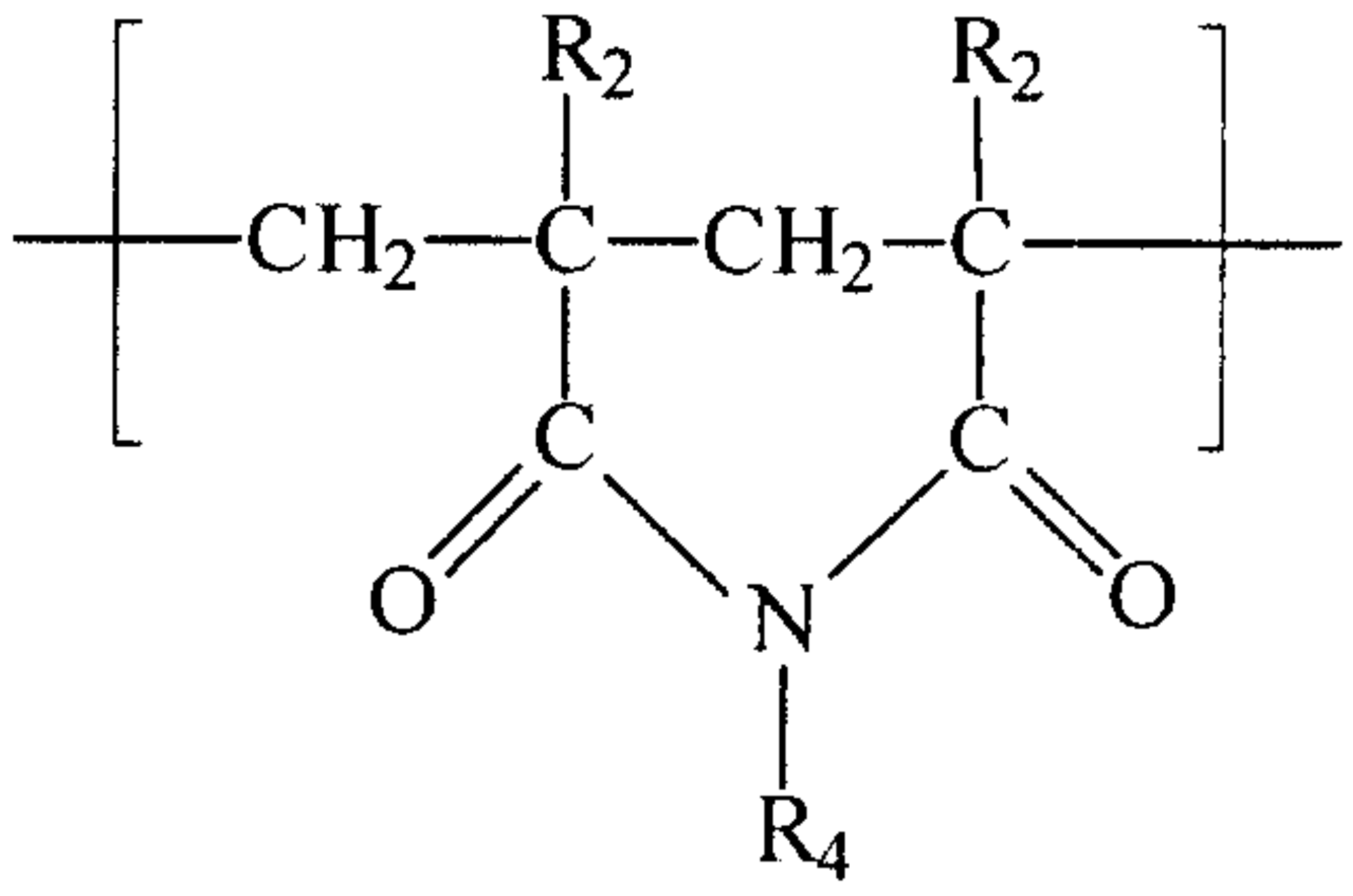
If necessary, the polyamides can be impact-modified. Suitable modifiers are, for example, ethylene/propylene or ethylene/propylene/diene copolymers (EP-A 295 076), polypentenylene, polyoctenylene or random or block copolymers made of alkenyl-aromatic compounds with aliphatic olefins or dienes (EP-A 261 748). Mention may furthermore be made of impact-modifying rubbers: core-shell rubbers having a tough, resilient core of (meth)acrylate, butadiene or styrene/butadiene rubber having glass transition temperatures T_g of < -10°C, where the core may be crosslinked. The shell can be built up from styrene and/or methyl methacrylate and/or further unsaturated monomers (DE-A 21 44 528 and 37 28 685). The proportion of impact-modifying component should be selected so that the desired properties are not impaired.

In addition to polyamide as component II.a., the intermediate layer according to II. also contains the component II.b. As component II.b., polyglutarimides are used which comprise the following basic building blocks:

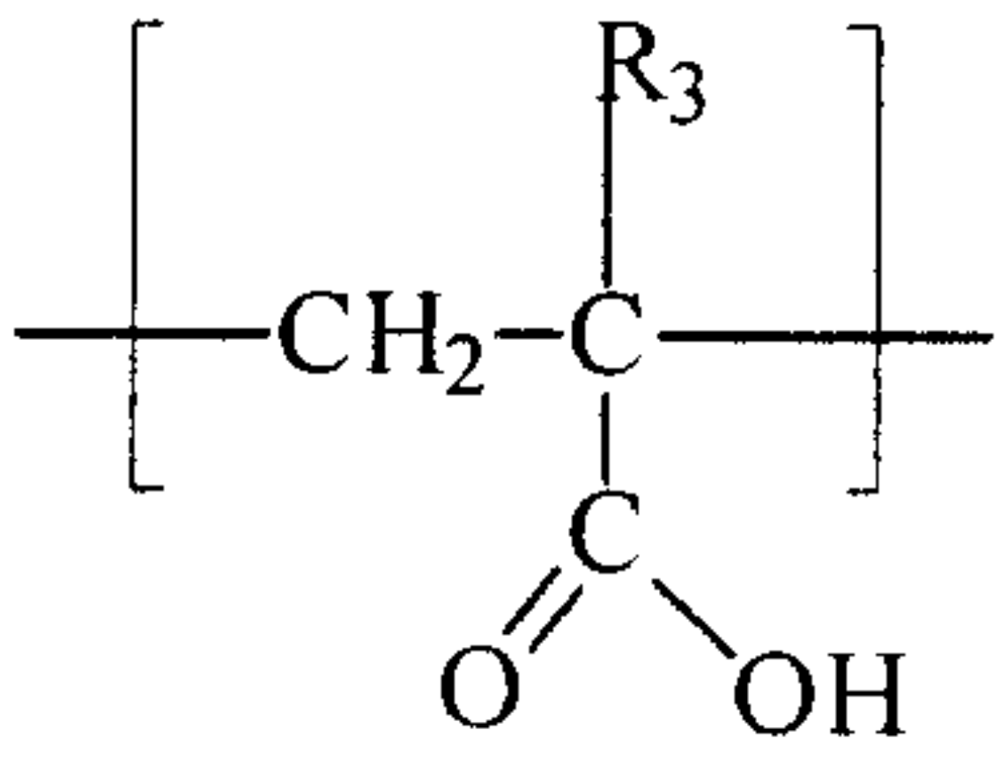
i) < 100% by weight, preferably from 10 to 60% by weight , of



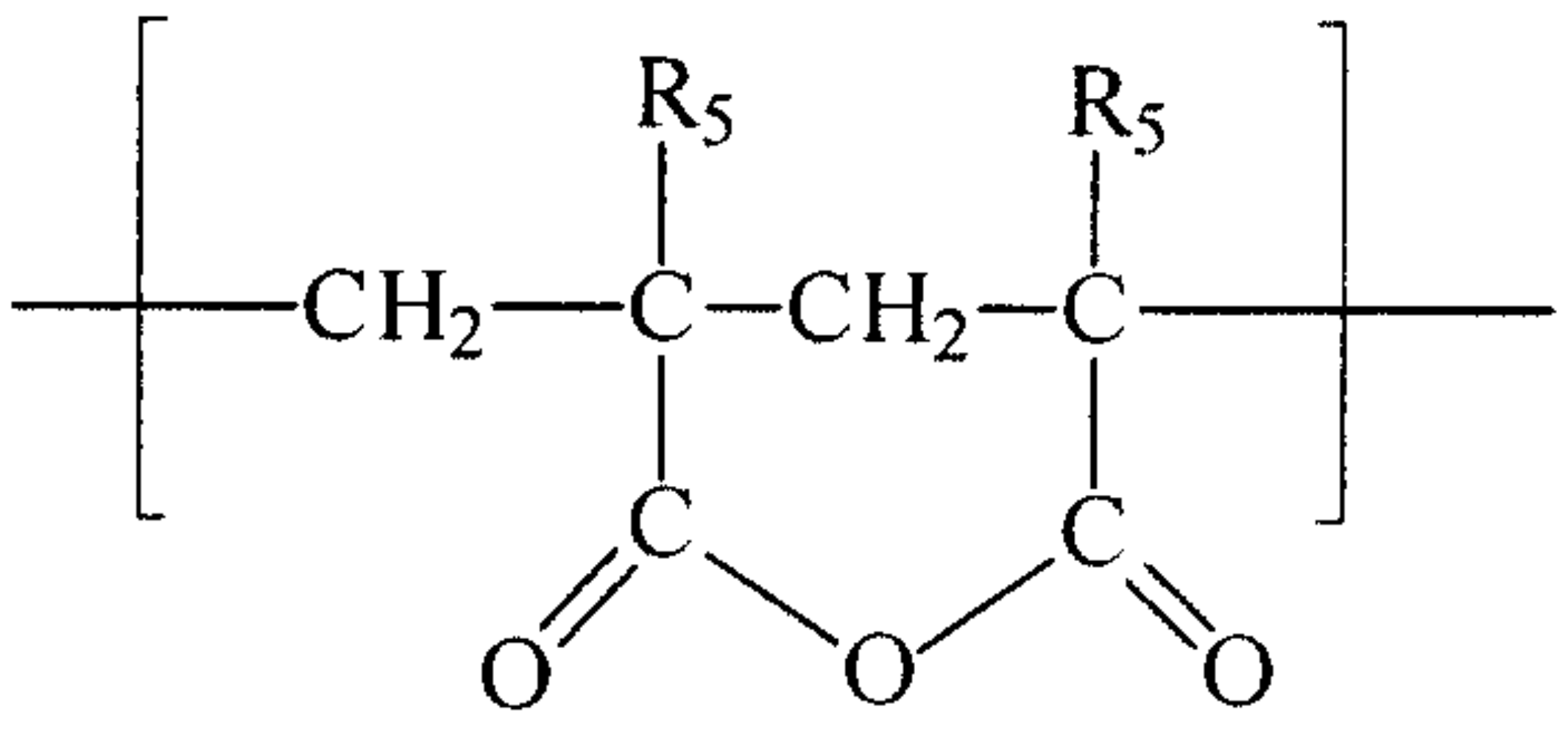
ii) < 100% by weight, preferably from 30 to 80% by weight, of



iii) < 20% by weight, preferably from 2 to 10% by weight, of



iv) from 1.2 to 20% by weight, preferably from 1.5 to 12% by weight, particularly preferably from 2 to 10% by weight, of



In the stated formulae

alkyl = methyl, ethyl, propyl, butyl, hexyl,
R_1 to R_5 = H, (C_nH_{2n+1})
and n = from 1 to 6,

where the substituents may be identical or different. Preference is given to those basic building blocks in which alkyl and R_1 to R_5 are methyl radicals.

The stated polymers of component II.b. are designated as polyglutarimides because they are poly(alkyl)acrylic esters in which two adjacent carboxylate groups have been reacted to form a cyclic imide. The imide formation is preferably carried out using ammonia or primary amines, such as methylamine. The products and their preparation are known (Hans. R. Kricheldorf, Handbook of Polymer Synthesis, Part A, Verlag Marcel Dekker Inc.; New York - Basel - Hong Kong, pp. 223 f.; H. G. Elias, Makromolekule [Macromolecules], Huthig und Wepf Verlag, Basel - Heidelberg - New York; US Patents 2,146,209 and 4,246,374).

The polyglutarimides used according to the invention generally have a melt flow index of < 30 g/10 min., preferably from 0.2 to 10 g/min.

To increase the low temperature impact toughness, the polyglutarimides can also contain appropriate modifiers. Examples are core/shell polymers having a polybutyl acrylate core and a shell of polymethyl methacrylate and/or polyglutarimide. In addition to the examples mentioned, further modifiers are possible.

The moulding compound for the layer according to II. is prepared by conventional and known processes by melt mixing the components II.a, and II.b. in a mixer having a good kneading action, such as, for example, a twin-screw kneader, at temperatures which depend on the melting points of components II.a. and II.b., in general at temperatures between 230 and 330°C.

The moulding compound for the layer according to II. can also be prepared directly in a feed extruder which is used for the production of the multilayer pipes in the coextrusion facility or injection-moulding facility used, so that the moulding compound for the layer according to II. can be processed into a layer of the multilayer pipe directly after its preparation, without further intermediate storage.

The components II.a. and II.b. are used in a weight ratio of from 40 to 90: from 50 to 10, preferably from 60 to 80: from 40 to 20.

The inner layer according to III. contains, in particular, polyvinylidene fluoride which is preferably used in plasticizer-free form. The preparation and structure of the polymer are known. (Hans R. Kricheldorf, Handbook of Polymer Synthesis, Part A, Verlag Marcel Dekker Inc., New York - Basel - Hong Kong, pp. 191 ff.; Kunststoff Handbuch [Plastics Handbook], 1st edition, vol. XI, Carl Hanser Verlag, Munich (1971), pp. 403 ff.).

Polymers based on polyvinylidene fluoride containing up to 40% by weight of other monomers may also be incorporated according to the invention. Examples of such additional monomers are: trifluoroethylene, ethylene, propene and hexafluoropropene.

The polyvinylidene fluoride of the invention generally has a melt flow index of < 17 g/10 min., preferably from 2 to 13 g/10 min. (DIN 53 735).

Preference is given to a layer according to III. which has been made electrically conductive (surface resistance $< 10^9\ \Omega$). Particular preference is given to an inner layer according to III. which comprises a. an outer layer based on polyvinylidene fluoride and b. an adjacent layer on the inside which has been made electrically conductive and has a surface resistance of $< 10^9\ \Omega$. The good electrical conductivity is achieved by addition of up to 15% by weight of, for example, conductive carbon black, carbon fibres or the like.

The moulding compounds for the layers according to I. to III. may include conventional auxiliaries and additives such as, for example, flameproofing agents, stabilizers, plasticizers, processing aids, viscosity improvers, fillers, in particular those for improving the conductivity, pigments or the like. The amount of said agents should be metered such that the desired properties are not seriously affected.

The manufacture of the multilayer pipes is carried out in a known manner, for example as described in the prior art further above. The pipes are preferably produced by coextrusion.

In the preferred embodiment, the multilayer pipes have a 3-layer structure - order of layers: I./II./III.

In a 3-layer pipe according to the invention having an external diameter of 8 mm and a total wall thickness of 1 mm, the layer thicknesses can be, for example, from the outside to the inside 0.8 mm/0.1 mm/0.1 mm. According to the invention, other distributions of layer thickness are also conceivable, for example with a thicker inner layer of, for example, 0.2 mm.

Furthermore, it is also possible to produce, besides a 3-layer pipe, other types of pipe having more than 3 layers. In addition, it is possible to use the same polyamide type for the layer according to I. and the component II.a. In a further embodiment, the material used for the layer according to I. may be of the same type as the component II.

The multilayer pipes of the invention have an outstandingly good resistance to, and a good barrier action with respect to diffusion of, (petro)chemical substances, solvents and fuels. In addition, the adjacent layers are adhesively bonded to one another, so that delamination of the adjacent layers does not occur, for example, on thermal expansion or flexing of a pipe.

The plastic pipes of the invention are preferred for use in the transport of (petro)chemical substances or in the motor vehicle sector for carrying brake, cooling and hydraulic fluids and also fuel. A further application of the multilayer pipes is the production from them of hollow bodies such as tanks or filling ports, in particular for the motor vehicle sector.

The stated parameters were determined by means of the following measurement methods.

The determination of the solution viscosity (relative viscosity η_{rel}) of the polyamides is carried out using a 0.5% strength by weight m-cresol solution at 25°C in accordance with DIN 53 727/ISO 307.

For the determination of the amino end groups, 1 g of the polyamides is dissolved in 50 ml of m-cresol at 25°C. The solution is titrated potentiometrically with perchloric acid.

For the determination of the carboxyl end groups in the polyamdies, 1 g of polycondensate is dissolved in 50 ml of benzyl alcohol under a blanket of nitrogen at 165°C. The dissolution time is a maximum of 20 minutes. The solution is titrated with a solution of KOH in ethylene glycol (0.05 mol of KOH/1) against phenolphthalein until the colour changes.

The determination of the melt flow index of the polyglutarimides is carried out at 230°C and under a load of 3.8 kg (DIN 53 735).

The determination of the melt flow index of the polyvinylidene fluorides is carried out at 230°C and under a load of 5 kg. (DIN 53 735).

The testing of the ease of mechanical separation at the interface is carried out using a metal wedge (edge angle: 5 degrees; loading weight: 2.5 kg); this test attempts to separate the material boundary layer to be tested. If separation takes place at the interface between the components, the adhesion is poor. If, by contrast, the separation takes place wholly or partly within one of the two components, good adhesion is present.

The determination of the diffusion of fuel components is carried out on pipes using a fuel mixture (fuel M 15:42.5 parts by volume of isooctane, 42.5 parts by volume of toluene and 15 parts by volume of methanol) at 23°C and 50% atmospheric humidity. The samples, having a length of 200 mm, are filled with the fuel mixture and are connected to a filled stock tank during the measurement. Diffusion is determined as the loss in weight by diffusion over time (measurement every 24 hours). The measure indicated is the weight loss recorded per unit area, measured when the diffusion process has achieved equilibrium, i.e. when the weight loss determined per 24 hours no longer changes with time.

Examples denoted by letters are not according to the invention.

Examples

A. Component I.

PA 1: Polyamide 12 (η_{rel}: 2.1; plasticizer content: 0; amino end group content: 9 mmol/kg; carboxyl end group content: 48 mmol/kg; VESTAMID® L 2140 - HÜLS AG)

PA 2: Polyamide 12 (η_{rel}: 2.1; plasticizer content per 100 parts by weight of polyamide: 15 parts by weight of N-n-butylbenzenesulphonamide; amino end group content: 9 mmol/kg; carboxyl end group content: 48 mmol/kg; VESTAMID® L 2124 - HÜLS AG)

PA 3: Polyamide 6.12 (η_{rel}: 1.9; plasticizer content: 0)

B. Component II.

The polyglutarimides comprise the basic building blocks designated as i) to iv) in Claim 8, where alkyl and R_1 to R_5 are methyl groups.

The mixtures for the component II. are prepared in a twin-screw kneader at a compound temperature of 280°C.

Composition of the polyglutarimides used in the examples:

	Amount	Polyglutarimide		Melt Flow Index [g/10 min.] polyglutarimide	
		A	B	A	B
i)	wt. %	18	57		
ii)	wt. %	77	30		
iii)	wt. %	3	3	0.4	0.4
iv)	wt. %	2	10		

Z 1: Mixture of

a. 50 parts by weight of polyamide 12 (η_{rel}: 2.1; plasticizer content: 0; amino end groups: 9 mmol/kg; carboxyl end groups: 48 mmol/kg; VESTAMID® L 2140, HÜLS AG)

and

b. 50 parts by weight of polyglutarmide A

Z 2: Mixture of

a. 70 parts by weight of polyamide 12 (η_{rel}: 2.1; plasticizer content: 0; amino end groups: 9 mmol/kg; carboxyl end groups: 48 mmol/kg; VESTAMID® L 2140, HÜLS AG)

and

b. 30 parts by weight of polyglutarimide A

Z 3: Mixture of

a. 70 parts by weight of polyamide 12 (η_{rel}: 1.8; plasticizer content: 0; amino end groups: 6

mmol/kg; carboxyl end groups: 73 mmol/kg; VESTAMID® L 1801, HÜLS AG)

and

b. 30 parts by weight of polyglutarimide B

Z 4: Mixture of

a. 60 parts by weight of polyamide 12 (η_{rel}: 2.1; plasticizer content per 100 parts by weight of polyamide: 15 parts by weight of N-n-butylbenzzensulphonamide; amino end groups: mmol/kg; carboxyl end groups: 48 mmol/kg; VESTAMID® L 2124, HÜLS AG)

and

b. 40 parts by weight of polyglutarimide A

Z 5: Mixture of

a. 80 parts by weight of polyamide 12 (η_{rel}: 2.1; plasticizer content per 100 parts by weight of polyamide: 15 parts by weight of N-n-butylbenzensulphonamide; amino end groups: 9

mmol/kg; carboxyl end groups: 48 mmol/kg; VESTAMID® L 2124, HÜLS AG)

and

b. 20 parts by weight of polyglutarimide B

C. Component III.

PVDF 1: Polyvinylidene fluoride (Melt flow index: 13 g/10 min.,DYFLOR® LE - HÜLS AG)

PVDF 2: Polyvinylidene fluoride (Melt flow index: 8.5 g/10 min., DYFLOR® EE - HÜLS AG)

PVDF 3: Polyvinylidene fluoride (Melt flow index: 8.5 g/10 min.; 6 parts by weight of commercial conductive carbon black (KETJEN BLACK™ EC 300 - AKZO) per 100 parts by weight of PVDF; DYFLOR® EE - HÜLS AG)

D. Production of the multilayer pipes

The pipes are produced in a laboratory extrusion facility having a five-layer tool (in the production of the pipes, the appropriate number of channels remains closed in each case). The barrel temperatures were 230°C (PA 1, PA 2, PA 3), 250°C

(PVDF 1, PVDF 2, PVDF 3), 260°C (Z 2, Z 3, Z 4, Z 5) and 280°C (Z 1).

The wall thickness of the 3-layer pipes is, from the outside to the inside: 0.75 mm/0.07 mm/0.18 mm. In the 2-layer pipes the wall thickness is, from the outside to the inside: 0.82 mm/0.18 mm, and the single-layer pipes have a wall thickness of 1 mm.

Table

Experiment	Outer layer according to I.	Inter-mediate layer according to II.	Inner layer according to III.	Diffusion [g/d m^2] at 23°C	Mechanically separable at interface after storage at 23°C		Mechanically separable at interface after storage in fuel*)	
					Layer I./II.	Layer II./III.	Layer I./II.	Layer II./III.
A	PA 1	-	-	30	-	-	-	-
B	PA 2	-	-	90	-	-	-	-
C	-	PA 1	PVDF 1	1.2	-	yes	-	yes
1	PA 2	Z 2	PVDF 1	1.2	no	no	no	no
2	PA 2	Z 3	PVDF 1	1.2	no	no	no	no
3	PA 1	Z 4	PVDF 2	1.1	no	no	no	no
4	PA 3	Z 1	PVDF 3	1.4	no	no	no	no
5	PA 2	Z 5	PVDF 3	1.5	no	no	no	no
6	Z 5	Z 5	PVDF 2	1.4	-	no	-	no
7	Z 3	Z 3	PVDF 2	1.6	-	no	-	no

*)Storage at 23°C for 5 days in standard fuel M 15

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A multilayer plastic pipe comprising at least:

   I. an outer layer

   II. an intermediate layer adjacent to the inner layer, which intermediate layer is made of a moulding compound based on a mixture of

      a. a polyamide, and

      b. a polyglutarimide

   III. an inner layer made of a moulding compound based on a polyvinylidene fluoride,

wherein the adjacent layers are adhesively bonded to one another.

2. A multilayer plastic pipe according to claim 1, wherein the outer layer is made of a moulding compound based on a polyamide

3. A multilayer plastic pipe according to claim 2, wherein the outer layer is made of a moulding compound based on a polyamide 12.

4. A multilayer plastic pipe according to claim 1, wherein the outer layer is made of a moulding compound based on a polyamide/polyglutarimide blend.

5. A multilayer plastic pipe according to claims 1 to 4, wherein the component for the outer layer and component II.a. are identical.

6. A multilayer plastic pipe according to claim 1, wherein the intermediate layer is made of a moulding compound based on a mixture of:

a. from about 40 to about 90 % by weight of a polyamide, and

b. from about 10 to about 60 % by weight of a polyglutarimide.

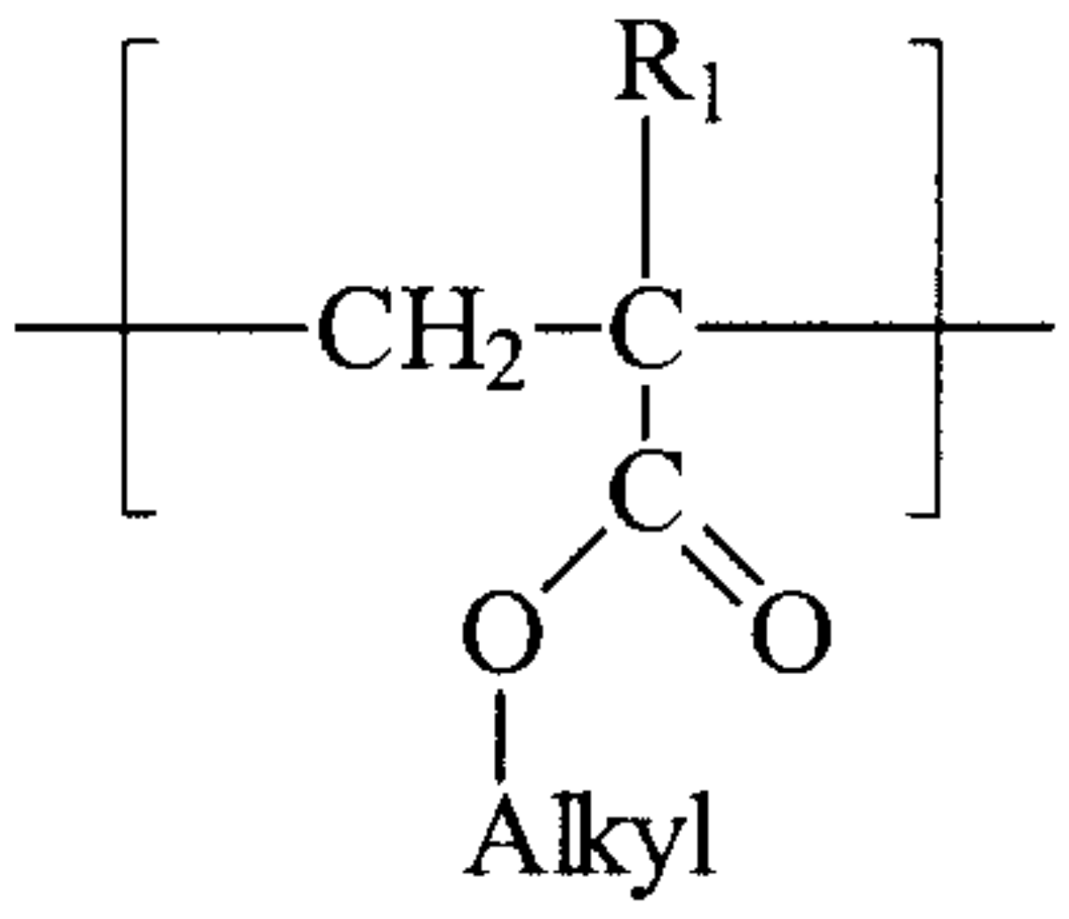
7. A multilayer plastic pipe according to claim 6, wherein the intermediate layer is made of a moulding compound based on a mixture of:

a. from about 60 to about 80 % by weight of a polyamide and

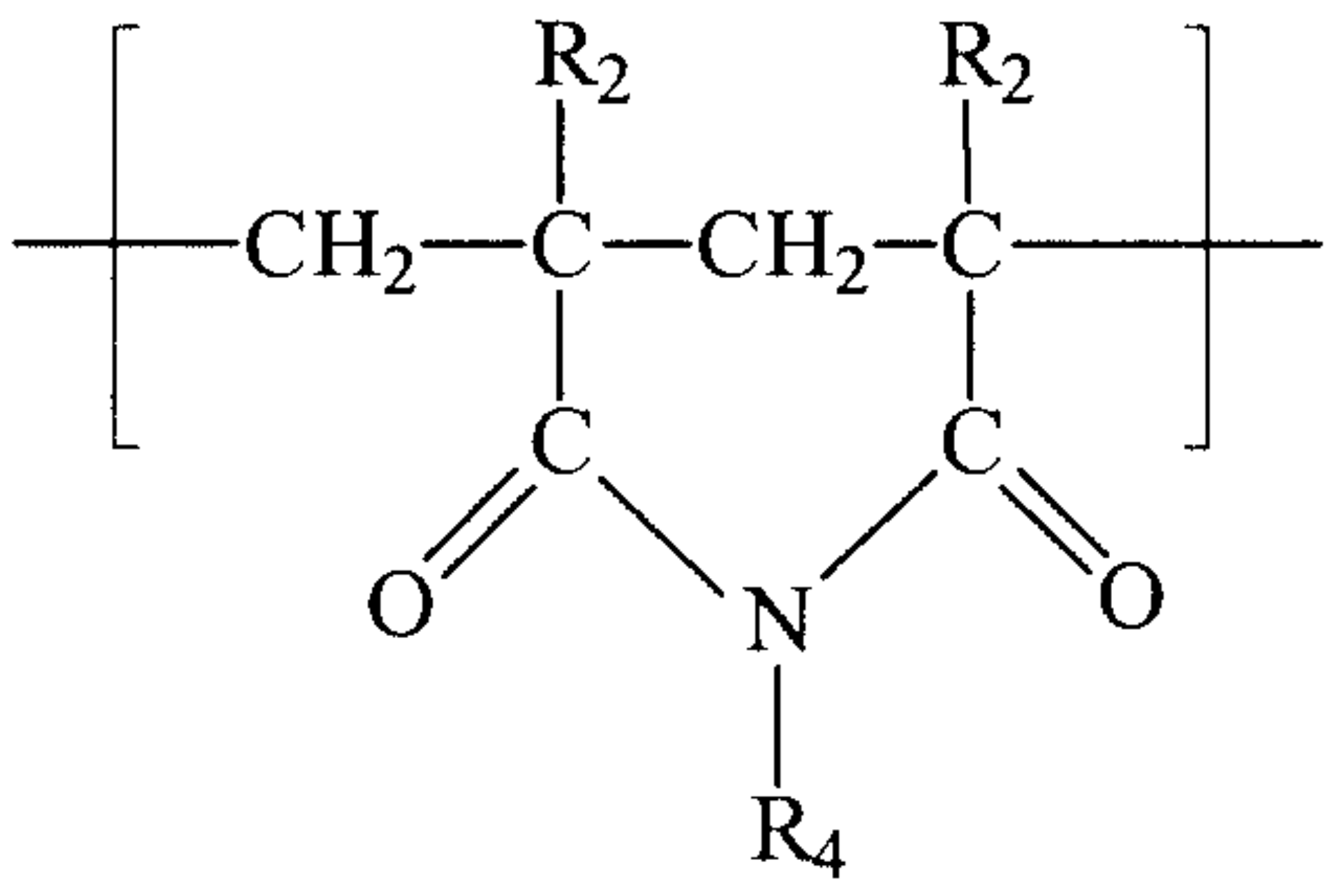
b. from about 20 to about 40 % by weight of a polyglutarimide.

8. A multilayer plastic pipe according to claim 1, wherein the component II.b. comprises the following basic building blocks:

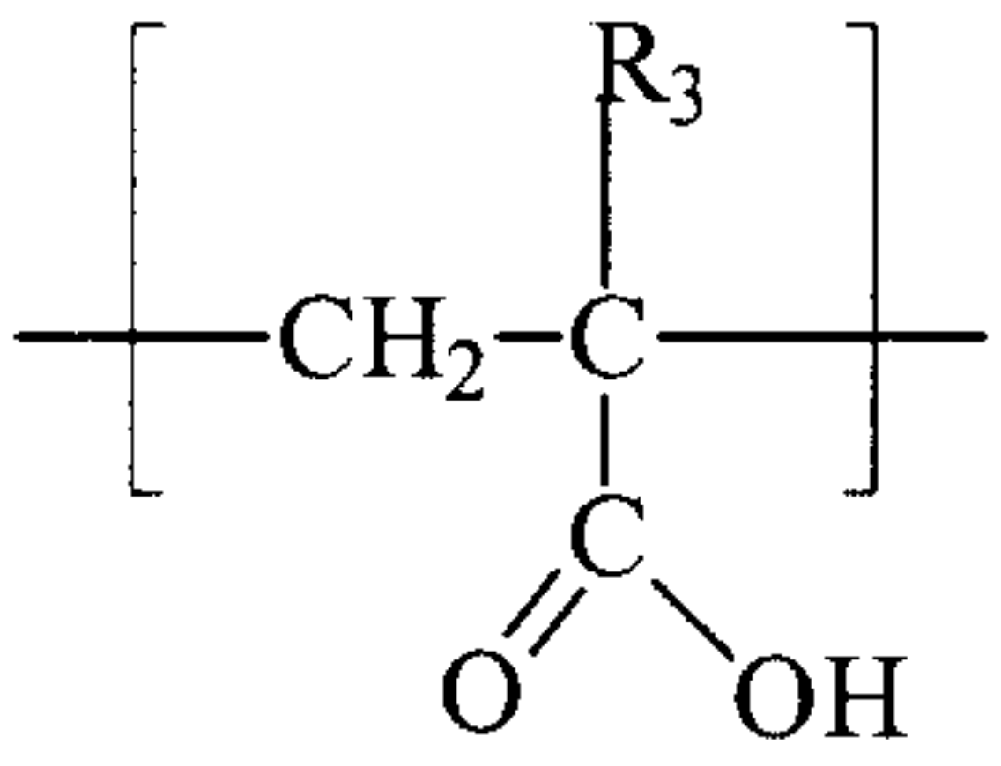
i) less than 100 % by weight of



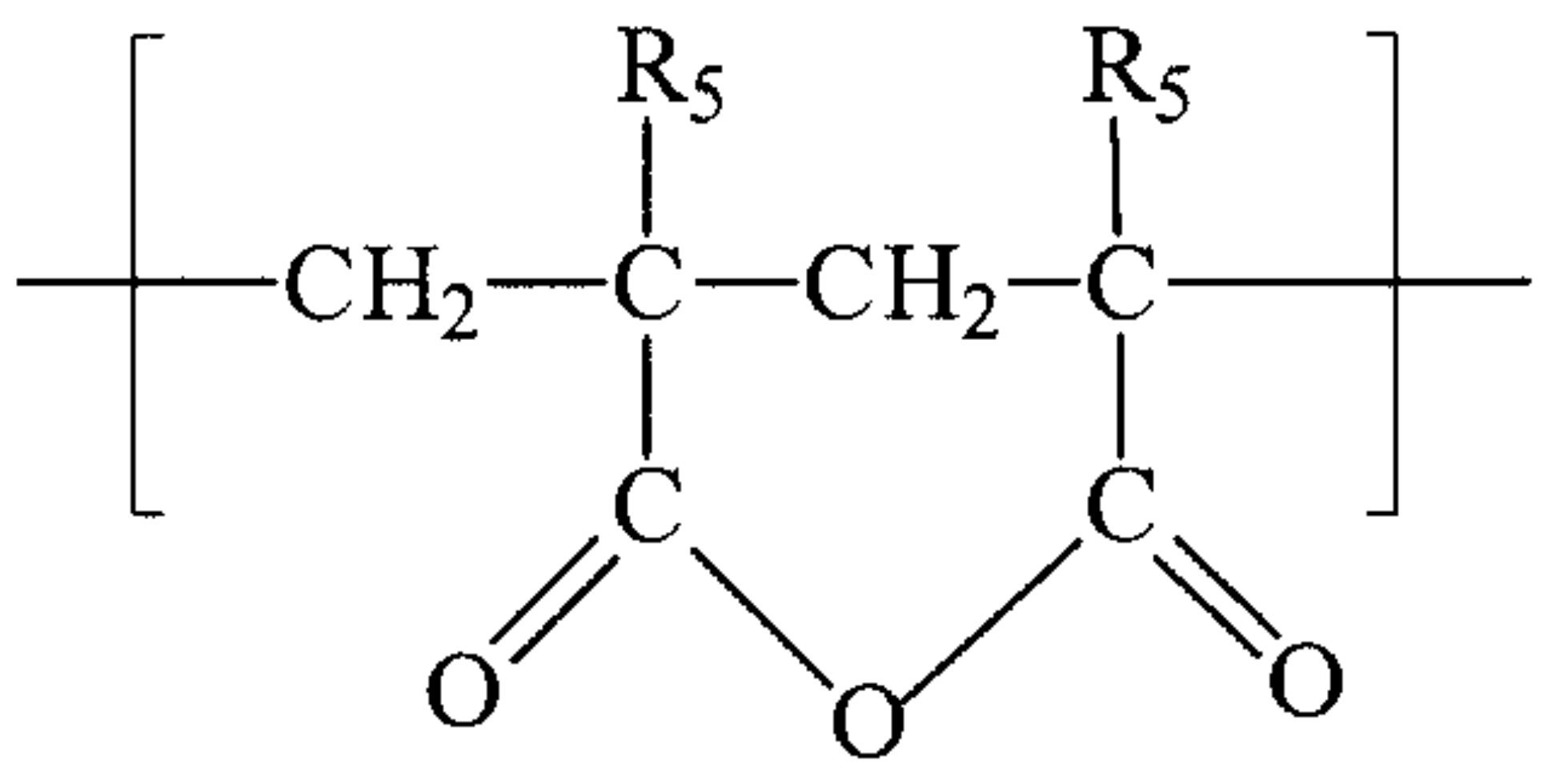
ii) less than 100 % by weight of



iii) less than about 20 % by weight of



iv) from about 1.2 to about 20 % by weight of

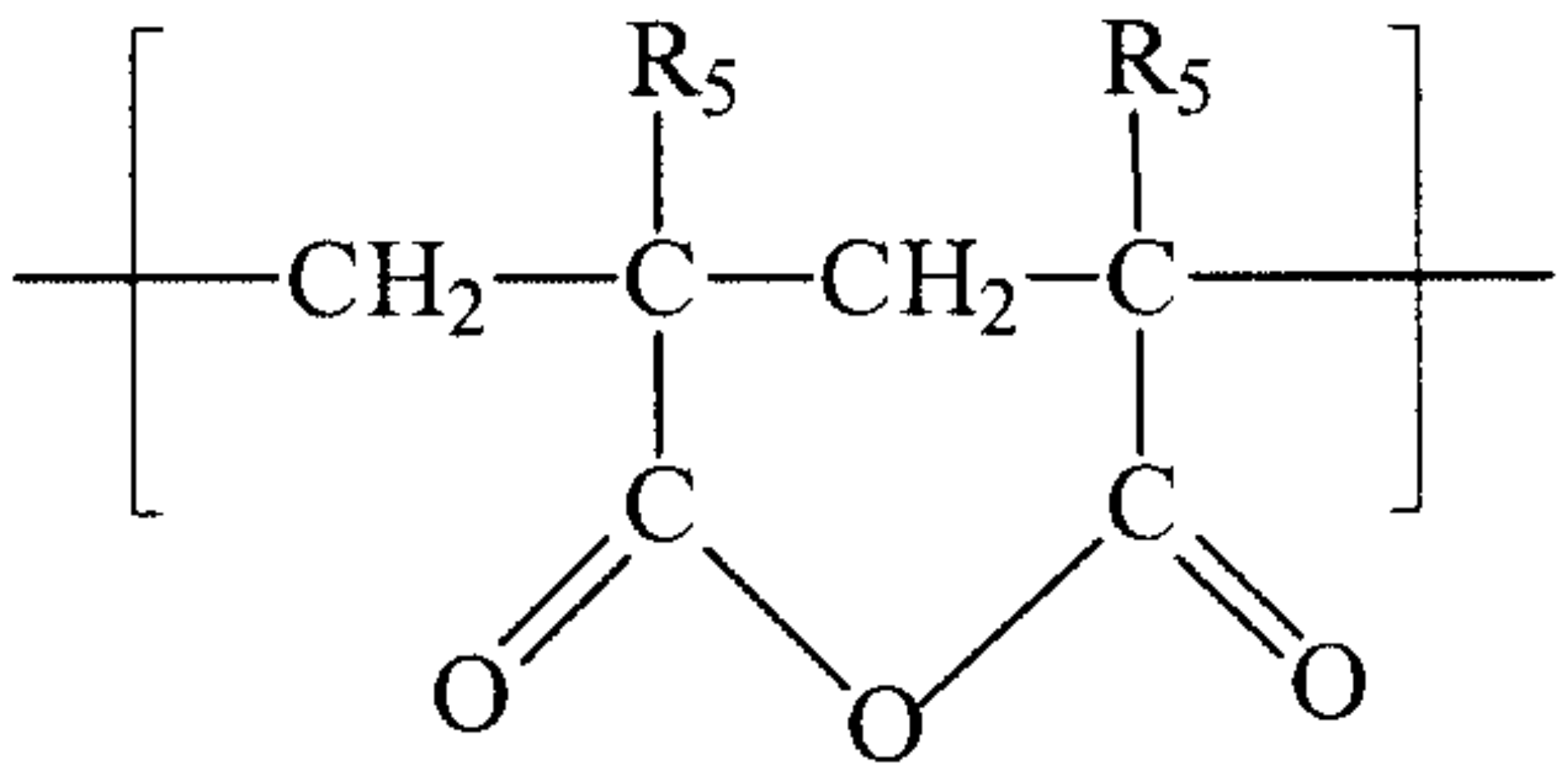


wherein Alkyl = methyl, ethyl, propyl, butyl, hexyl, R_1 to R_5 = H, (C_nH_{2n+1}) and n = from 1 to 6

and the substituents may be identical or different.

9. A multilayer plastic pipe according to claim 8, wherein the component II.b. comprises the following basic building blocks:

v) from about 2 to about 10 % by weight of



where R_5 = H, (C_nH_{2n+1}) and n = from 1 to 6.

11. A multilayer plastic pipe according to claim 8, 9 or 10, wherein Alkyl and R_1 to R_5 are methyl groups.

12. A multilayer plastic pipe according to claim 1, wherein the inner layer comprises a moulding compound based on a polyvinylidene fluoride having a melt flow index of less than about 17 g/10 min.

13. A multilayer plastic pipe according to claim 12, wherein the inner layer comprises a moulding compound based on a polyvinylidene fluoride having a melt index from about 2 to about 13 g/10 min.

14. A multilayer plastic pipe according to claim 1, wherein the inner layer comprises a moulding compound based on a polyvinylidene fluoride copolymer.

15. A multilayer plastic pipe according to claim 1, wherein the inner layer is made electrically conductive and has a surface resistance of less than about $10^9\Omega$.

16. A multilayer plastic pipe according to claim 1, wherein the inner layer consists of:

   a. an outer layer based on a polyvinylidene fluoride, and
   b. an adjacent layer on the inside, which layer is electrically conductive and has a surface resistance of less than about $10^9\Omega$.

17. Use of the multilayer plastic pipe according to any one of claims 1 to 10 and 12 to 16 for the transport of (petro)chemical substances.

18. Use according to claim 17 in the motor vehicle sector for carrying brake, cooling and hydraulic fluids and also fuel.

19. Use of the multilayer plastic pipe according to any one of claims 1 to 10 and 12 to 16 for the production of hollow bodies.

20. Use according to claim 19 for the production of filling ports or tanks in the motor vehicle sector.

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