

Tetraisopentyl esters of butanetetracarboxylic acid, production thereof and use thereof as plasticizers

5 The present invention relates to tetraisopentyl esters of butanetetracarboxylic acid, to the production thereof and to the use thereof as plasticizers or as part of a plasticizer composition for polymers. Also disclosed are plasticizer compositions containing the tetraisopentyl esters of butanetetracarboxylic acid and plastics compositions containing the tetraisopentyl esters of butanetetracarboxylic acid.

10 In many fields of application plastics/polymers are admixed with plasticizers or plasticizer compositions to improve processability and/or to adapt application-relevant properties. Due to their advantageous properties, compounds from the group of phthalates, in particular diethylhexyl phthalate (DEHP), diisononyl phthalate (DINP) and diisodecyl phthalate (DIDP), still remain among the most important plasticizers for plastics/polymers, especially for PVC and vinyl chloride-
15 containing copolymers. Due to discourse about possible toxicological effects of this class of substances, alternatives for phthalate-based plasticizers have been sought for many years.

Various compounds are discussed as alternative plasticizers, these including inter alia alkyl esters of butanetetracarboxylic acid which are already known to those skilled in the art from US
20 2011/0257317 A1 for example. The alkyl esters of butanetetracarboxylic acid disclosed therein have a maximum proportion of alkyl radicals branched at the beta position of 40%.

Having regard to tetraisopentyl esters of butanetetracarboxylic acid it has now been found that, surprisingly, improved properties occur at a certain molar proportion of 2-methylbutyl radicals
25 based on the total isomeric pentyl radicals. The underlying problem addressed by the present invention was accordingly that of providing tetraisopentyl esters of butanetetracarboxylic acid with improved properties.

The underlying problem is solved by the mixture of tetraisopentyl esters of 1,2,3,4-
30 butanetetracarboxylic acid according to Claim 1. Preferred embodiments are specified in the dependent claims.

In the context of the present invention, the terms "isopentyl", "isopentyl radicals" or the like are used. This emphasizes that the esters according to the invention contain various pentyl isomers, in
35 particular 2-methylbutyl and/or 3-methylbutyl and/or n-pentyl. The terms "isopentyl", "isopentyl radicals" or the like are therefore to be understood as being synonymous with the term "pentyl" and do not refer to a single specific C5-alkyl group.

The present invention accordingly relates to a mixture of tetraisopentyl esters of 1,2,3,4-butanetetracarboxylic acid, wherein 6 to 12 mol% of the isopentyl radicals in the mixture are 2-methylbutyl radicals, 88 to 94 mol% of the isopentyl radicals in the mixture are n-pentyl radicals and 0 to 4 mol% of the isopentyl radicals in the mixture are 3-methylbutyl radicals. The reported percentages in each case refer to the total isopentyl radicals in the mixture. A preferred embodiment of the present invention provides that in the mixture of tetraisopentyl esters of 1,2,3,4-butanetetracarboxylic acid 6 to 10 mol% of the isopentyl radicals in the mixture are 2-methylbutyl radicals, 90 to 94 mol% of the isopentyl radicals in the mixture are n-pentyl radicals and 0 to 2 mol% of the isopentyl radicals in the mixture are 3-methylbutyl radicals. A particularly preferred embodiment of the present invention provides that in the mixture of tetraisopentyl esters of 1,2,3,4-butanetetracarboxylic acid 7 to 9 mol% of the isopentyl radicals in the mixture are 2-methylbutyl radicals, 91 to 93 mol% of the isopentyl radicals in the mixture are n-pentyl radicals and 0 to 2 mol% of the isopentyl radicals in the mixture are 3-methylbutyl radicals.

It is apparent that the inventive mixtures having a proportion of 6 to 12 mol% of 2-methylbutyl radicals are practically as good as mixtures containing only n-pentyl radicals. However, the advantage in the present case is that the output from the hydroformylation of butenes and subsequent hydrogenation can be used for the production of the ester mixtures. In order to obtain a pure n-pentyl ester this output would need to be subjected to a complex and costly distillation to obtain n-pentanol and the pure n-pentanol then used to produce the ester.

It is preferable according to the invention for as few 3-methylbutyl radicals as possible to be present in the mixture. It is accordingly preferable when less than 1 mol% of the isopentyl radicals in the mixture are 3-methylbutyl radicals and particularly preferable when less than 0.5 mol% of the isopentyl radicals in the mixture are 3-methylbutyl radicals.

The inventive mixture of tetraisopentyl esters of 1,2,3,4-butanetetracarboxylic acid may be produced by esterification of the 1,2,3,4-butanetetracarboxylic acid with a suitable isopentanol mixture. In this context isopentanol mixture is to be understood as meaning that this mixture contains at least 2-methylbutanol and n-pentanol and/or 3-methylbutanol. It should understandably be ensured during the esterification that the mixture contains sufficient 2-methylbutanol to obtain the required amount of 2-methylbutyl radicals in the ester formed. As is well known the selection of suitable isopentanol mixtures may be effected by reaction and analysis of the esters formed.

The esterification is preferably carried out in the presence of a catalyst. Known catalyst systems suitable for esterification may in principle be used to this end. Suitable catalysts for the esterification to produce the inventive tetraisopentyl esters of 1,2,3,4-butanetetracarboxylic acid are titanate catalysts, for example tetra-n-butyl titanate, zirconates or sulfonic acids.

The esterification to produce the esters according to the invention is preferably carried out at a temperature of 120°C to 250°C, more preferably at a temperature of 140°C to 230°C, particularly preferably at a temperature of 160°C to 215°C. The pressure during the esterification should preferably not be excessively high since this would increase the boiling temperature and thus also the esterification temperature and might favour increased formation of byproducts. The pressure during the esterification is therefore 3 bar absolute or less, particularly preferably not less than 0.5 bar absolute.

During an esterification the reaction of the acid group with an alcohol forms water. This water is also called water of reaction. In a preferred embodiment of the present invention at least a portion of the water of reaction formed is separated during the ongoing reaction. This can inter alia shift the equilibrium of the reaction in the right direction.

The progress of the esterification reaction can be monitored by monitoring a parameter. The acid number or the amount of water may be monitored for example. Monitoring by gas chromatography, where the proportion of reactants and/or products may be determined, is also possible. It is also possible here to employ online analytical techniques such as for example NIR spectroscopy.

Once the reaction has progressed to a sufficient extent the reaction may be terminated. This may be done for example by addition of a base, for example aqueous sodium hydroxide solution. This generally destroys the catalyst. A person skilled in the art is well aware of this. The reaction solution may subsequently be worked up with known processes, for example by thermal separation.

The inventive mixture of tetraisopentyl esters of 1,2,3,4-butanetetracarboxylic acid has advantageous properties when used as a plasticizer for polymers. A further subject of the present invention is therefore the use of the mixture of tetraisopentyl esters of 1,2,3,4-butanetetracarboxylic acid as a plasticizer for polymers. Suitable polymers are specified below, preference being given to PVC or vinyl chloride-containing copolymers.

A further subject of the present invention is a plasticizer composition which contains a further plasticizer in addition to the mixture of tetraisopentyl esters of 1,2,3,4-butanetetracarboxylic acid. Depending on the intended application, the plasticizer composition may contain one or more additional plasticizers that are especially distinct from the inventive mixture of tetraisopentyl esters of 1,2,3,4-butanetetracarboxylic acid to specifically adjust the properties of the resulting plasticizer composition. However, in a particularly preferred embodiment the plasticizer composition comprises less than 5% by weight, more preferably less than 0.5% by weight, particularly preferably less than 0.1% by weight, of phthalates, i.e. esters of ortho-phthalic acid.

The additional plasticizers in the inventive plasticizer composition may be selected from the group consisting of adipates, benzoates, for example monobenzoates or glycol dibenzoates, chlorinated hydrocarbons (so-called chloroparaffins), citrates, cyclohexanedicarboxylates, epoxidized fatty acid esters, epoxidized vegetable oils, epoxidized acylated glycerides, furandicarboxylates, phosphates, succinates, sulfonamides, sulfonates, terephthalates, isophthalates, trimellitates and oligomeric or polymeric esters based on adipic acid, succinic acid or sebacic acid. In a preferred embodiment of the present invention, the plasticizer composition comprises a further plasticizer selected from the group consisting of alkyl benzoates, alkylsulfonic esters of phenol, dialkyl adipates, glycerol esters, C4-C6-acids of polyols, trialkyl citrates, acetylated trialkyl citrates, glycol dibenzoates, trialkyl esters of trimellitic acid, dialkyl terephthalates, dialkyl phthalates, dialkyl isophthalates, esters of furandicarboxylic acid, dialkanoyl esters of dianhydrohexitols (for example isosorbide), epoxidized fatty acid alkyl esters, polymer plasticizers, for example polyadipates, and dialkyl esters of 1,2-, 1,3- or 1,4-cyclohexanedicarboxylic acid.

In a further preferred embodiment the further plasticizer present in the plasticizer composition is selected from the group consisting of C8- to C13-alkyl benzoates, C4- to C10-dialkyl adipates, pentaerythritol tetravalerate, acetylated trialkyl citrates having C4 to C9-alkyl groups, C4- to C10-trialkyl trimellitates, C4- to C9-dialkyl terephthalates, C4- to C13-dialkyl phthalates, especially C9- to C13-dialkyl phthalates and C4- to C10-dialkyl esters of 1,2-, 1,3- or 1,4-cyclohexanedicarboxylic acid.

A further subject of the present invention is therefore a plastics composition containing the inventive mixture of tetraisopentyl esters of 1,2,3,4-butanetetracarboxylic acid or the plasticizer composition and one or more polymers.

Suitable polymers are preferably selected from the group consisting of PVC, homo- or copolymers based on ethylene, propylene, butadiene, vinyl acetate, glycidyl acrylate, glycidyl methacrylate, ethyl acrylate, butyl acrylate or methacrylate with alkoxy radicals of branched or unbranched alcohols having one to ten carbon atom(s), acrylonitrile or cyclic olefins, polyvinylidene chloride (PVDC), polyacrylates, in particular polymethyl methacrylate (PMMA), polyalkyl methacrylate (PAMA), polyureas, silylated polymers, fluoropolymers, especially polyvinylidene fluoride (PVDF), polytetrafluoroethylene (PTFE), polyvinyl acetate (PVAc), polyvinyl alcohol (PVA), polyvinyl acetals, especially polyvinyl butyral (PVB), polystyrene polymers, especially polystyrene (PS), expandable polystyrene (EPS), acrylonitrile-styrene-acrylate (ASA), styrene-acrylonitrile (SAN), acrylonitrile-butadiene-styrene (ABS), styrene-maleic anhydride copolymer (SMA), styrene-methacrylic acid copolymer, polyolefins, especially polyethylene (PE) or polypropylene (PP), thermoplastic polyolefins (TPO), polyethylene-vinyl acetate (EVA), polycarbonates, polyethylene terephthalate (PET), polybutylene terephthalate (PBT), polyoxymethylene (POM), polyamide (PA), polyethylene glycol (PEG), polyurethane (PU), thermoplastic polyurethane (TPU), polysulfides (PSu),

biopolymers, especially polylactic acid (PLA), polyhydroxybutyral (PHB), polyhydroxyvaleric acid (PHV), polyesters, starch, cellulose and cellulose derivatives, especially nitrocellulose (NC), ethylcellulose (EC), cellulose acetate (CA), cellulose acetate/butyrate (CAB), rubber and silicones.

5 In a preferred embodiment at least one polymer or preferably at least 90% by weight of the two or more polymers in the plasticizer composition is/are selected from the group consisting of polyvinyl chloride (PVC), polyalkyl methacrylate (PAMA), polyvinyl butyral (PVB), polyurethane, polysulfide, polylactic acid (PLA), polyhydroxybutyral (PHB), nitrocellulose and copolymers of vinyl chloride with vinyl acetate or with butyl acrylate. PVC is particularly preferred.

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The amount of the inventive mixture of tetraisopentyl esters of 1,2,3,4-butanetetracarboxylic acid or of the plasticizer composition in the plastics composition is preferably 5 to 150 parts by mass, preferably 10 to 120 parts by mass, particularly preferably 15 to 110 parts by mass and very particularly preferably 20 to 100 parts by mass per 100 parts by mass of polymer. Also conceivable
15 however are compositions containing one or more polymers which comprise less than 20 parts by mass of the inventive tetraisopentyl esters of 1,2,3,4-butanetetracarboxylic acid per 100 parts by mass of the polymer.

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Specific compositions/mixtures of plasticizers comprising the inventive mixtures of tetraisopentyl esters of 1,2,3,4-butanetetracarboxylic acid that are preferred in the context of the present invention are reported below.

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A preferred subject of the present invention is a plastics composition comprising the mixture of tetraisopentyl esters of 1,2,3,4-butanetetracarboxylic acid and diethylhexyl terephthalate (DEHT or DOTP) and at least one polymer, preferably PVC.

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A further preferred subject of the present invention is a plastics composition comprising the mixture of tetraisopentyl esters of 1,2,3,4-butanetetracarboxylic acid and 1,2- or 1,4-cyclohexanedicarboxylic esters, in particular the corresponding diisononyl or di-2-ethylhexyl esters, and at least one polymer, preferably PVC.

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Also preferred is a plastics composition comprising the mixture of tetraisopentyl esters of 1,2,3,4-butanetetracarboxylic acid and trialkyl esters of trimellitic acid in which the alkyl radicals comprise 4 or more carbon atoms, preferably 5, 8, 9 or 10 carbon atoms, and at least one polymer, preferably PVC.

Also preferred is a plastics composition comprising the mixture of tetraisopentyl esters of 1,2,3,4-butanetetracarboxylic acid and trialkyl esters of 1,2,4-cyclohexanetricarboxylic acid in which the

alkyl radicals comprise 4 or more carbon atoms, preferably 5, 8, 9 or 10 carbon atoms, and at least one polymer, preferably PVC.

5 A further preferred subject of the present invention is a plastics composition containing the mixture of tetraisopentyl esters of 1,2,3,4-butanetetracarboxylic acid and a rapidly gelating plasticizer selected from the group consisting of dibutyl terephthalate, di(iso)-pentyl terephthalate, isodecyl benzoate, isononyl benzoate, acetyltributyl citrate, tributyl citrate, dipropylene glycol dibenzoate, diethylene glycol dibenzoate, triethylene glycol dibenzoate and mixtures of two or more thereof, and at least one polymer, preferably PVC.

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The inventive plastics composition is preferably a constituent of an adhesive, of a sealing composition, of a coating composition, of a lacquer, of a paint, of a plastisol, of a dryblend, of a foam, of a synthetic leather, of a floor covering, particularly the topcoat or foam layer thereof, of a roofing membrane, of an underbody protection, of a fabric coating, of a cable, of a wire insulation, 15 of a hose, of an extruded article, of a film, of an article in the field of automotive interiors, of a wallpaper, of an ink, of a toy, of a contact sheet, of a foodstuffs packaging or of a medical article, especially of a tube or of a blood bag.

A further subject of the present invention is therefore the use of the plastics composition in 20 adhesives, sealing compositions, coating compositions, lacquers, paints, plastisols, foams, synthetic leathers, floor coverings, particularly the topcoat or foam layer, roofing membranes, underbody protection, fabric coatings, cables, wire insulation, hoses, extruded articles, films, in the field of automotive interiors, in wallpapers, inks, toys, contact sheets, foodstuffs packaging or medical articles, especially in tubes or blood bags.

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It has already been mentioned that the terms "isopentyl", "isopentyl radicals" or the like are to be understood as being synonymous with the term "pentyl" and do not refer to a single specific C5-alkyl group. In this respect, the individual inventive subjects of the present invention could also be described as follows:

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1. Mixture of tetrapentyl esters of 1,2,3,4-butanetetracarboxylic acid, wherein 6 to 12 mol% of the pentyl radicals in the mixture are 2-methylbutyl radicals, 88 to 94 mol% of the pentyl radicals in the mixture are n-pentyl radicals and 0 to 4 mol% of the pentyl radicals in the mixture are 3-methylbutyl radicals.

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2. Mixture according to subject 1, wherein 6 to 10 mol% of the pentyl radicals in the mixture are 2-methylbutyl radicals, 90 to 94 mol% of the pentyl radicals in the mixture are n-pentyl radicals and 0 to 2 mol% of the pentyl radicals in the mixture are 3-methylbutyl radicals.

3. Mixture according to subject 1, wherein 7 to 9 mol% of the pentyl radicals in the mixture are 2-methylbutyl radicals, 91 to 93 mol% of the pentyl radicals in the mixture are n-pentyl radicals and 0 to 2 mol% of the pentyl radicals in the mixture are 3-methylbutyl radicals.
- 5 4. Mixture according to any of subjects 1 to 3, wherein less than 1 mol% of the pentyl radicals in the mixture are 3-methylbutyl radicals.
5. Mixture according to subject 4, wherein less than 0.5 mol% of the pentyl radicals in the mixture are 3-methylbutyl radicals.
- 10 6. Process for producing the mixture of tetrapentyl esters of 1,2,3,4-butanetetracarboxylic acid according to any of subjects 1 to 5, wherein the producing is carried out either by esterification of 1,2,3,4-butanetetracarboxylic acid with a pentanol mixture or by transesterification of the tetramethyl ester of 1,2,3,4-butanetetracarboxylic acid with a pentanol mixture.
- 15 7. Process according to subject 6, wherein the water of reaction formed during the esterification is separated during the reaction.
8. Process according to subject 6 or 7, wherein the esterification is performed at a
20 temperature in the range from 120°C to 250°C.
9. Use of the mixture of tetrapentyl esters of 1,2,3,4-butanetetracarboxylic acid according to any of subjects 1 to 5 as a plasticizer for polymers, in particular for PVC or vinyl chloride-containing copolymers.
- 25 10. Plasticizer composition containing the mixture of tetrapentyl esters of 1,2,3,4-butanetetracarboxylic acid according to any of subjects 1 to 5 and at least one further plasticizing compound.
- 30 11. Plasticizer composition according to subject 10, wherein the further plasticizing compound is selected from the group consisting of adipates, benzoates, for example monobenzoates or glycol dibenzoates, chlorinated hydrocarbons (so-called chloroparaffins), citrates, cyclohexanedicarboxylates, epoxidized fatty acid esters, epoxidized vegetable oils, epoxidized acylated glycerides, furandicarboxylates, phosphates, succinates, sulfonamides, sulfonates,
35 terephthalates, trimellitates and oligomeric or polymeric esters based on adipic acid, succinic acid or sebacic acid.

12. Plasticizer composition according to subject 10 or 11, wherein the plasticizer composition contains less than 5% by weight, more preferably less than 0.5% by weight, particularly preferably less than 0.1% by weight, of phthalates.
- 5 13. Plastics composition containing the mixture of tetrapentyl esters of 1,2,3,4-butanetetracarboxylic acid according to any of subjects 1 to 5 or the plasticizer composition according to any of subjects 10 to 12 and one or more polymers.
- 10 14. Plastics composition according to subject 13, wherein the one or more polymers are selected from the group consisting of PVC, homo- or copolymers based on ethylene, propylene, butadiene, vinyl acetate, glycidyl acrylate, glycidyl methacrylate, ethyl acrylate, butyl acrylate or methacrylate with alkoxy radicals of branched or unbranched alcohols having one to ten carbon atom(s), acrylonitrile or cyclic olefins, polyvinylidene chloride (PVDC), polyacrylates, in particular polymethyl methacrylate (PMMA), polyalkyl methacrylate (PAMA), polyureas, silylated polymers, 15 fluoropolymers, especially polyvinylidene fluoride (PVDF), polytetrafluoroethylene (PTFE), polyvinyl acetate (PVAc), polyvinyl alcohol (PVA), polyvinyl acetals, especially polyvinyl butyral (PVB), polystyrene polymers, especially polystyrene (PS), expandable polystyrene (EPS), acrylonitrile-styrene-acrylate (ASA), styrene-acrylonitrile (SAN), acrylonitrile-butadiene-styrene (ABS), styrene-maleic anhydride copolymer (SMA), styrene-methacrylic acid copolymer, polyolefins, especially 20 polyethylene (PE) or polypropylene (PP), thermoplastic polyolefins (TPO), polyethylene-vinyl acetate (EVA), polycarbonates, polyethylene terephthalate (PET), polybutylene terephthalate (PBT), polyoxymethylene (POM), polyamide (PA), polyethylene glycol (PEG), polyurethane (PU), thermoplastic polyurethane (TPU), polysulfides (PSu), biopolymers, especially polylactic acid (PLA), polyhydroxybutyral (PHB), polyhydroxyvaleric acid (PHV), polyesters, starch, cellulose and 25 cellulose derivatives, especially nitrocellulose (NC), ethylcellulose (EC), cellulose acetate (CA), cellulose acetate/butyrate (CAB), rubber and silicones.
15. Use of the plastics composition according to subject 13 or 14 in adhesives, sealing compositions, coating compositions, lacquers, paints, plastisols, foams, synthetic leathers, floor 30 coverings (for example the topcoat), roofing membranes, underbody protection, fabric coatings, cables, wire insulation, hoses, extruded articles, films, in the field of automotive interiors, in wallpapers, inks, toys, contact sheets, foodstuffs packaging or medical articles, for example tubes or blood bags.
- 35 The invention is elucidated hereinbelow by reference to examples. The examples are intended to be illustrative and are not to be understood as being limiting.

Examples

Synthesis of the mixture of tetraisopentyl esters of 1,2,3,4-butanetetracarboxylic acid

5 An apparatus was charged with 5 mol of 1,2,3,4-butanetetracarboxylic acid (Alfa Aesar, purity: > 98 %) and corresponding quantities of the alcohols 2-methylbutanol, n-pentanol and 3-methylbutanol (2-methylbutanol: Sigma Aldrich, purity $\geq$ 99%; 3-methylbutanol: Honeywell, purity $\geq$ 98.5%; n-pentanol: Honeywell, purity $\geq$ 99%). 3.4 g of tetra-n-butyl titanate (0.01 mol, Sigma Aldrich, purity: > 97%) were added thereto as catalyst and the reaction was commenced. The reaction was carried
10 out with nitrogen sparging. The reactants were slowly heated to a reaction temperature of 200°C. Once the reaction temperature had been reached additional alcohol was metered in. It was ensured during metered addition that the reaction temperature did not fall below 200°C.

In the course of the esterification, 360 ml of water was produced (20 mol of water of reaction). The
15 water formed during the reaction was continuously removed via a water trap. Once 360 ml of water of reaction had been formed the acid number (AN) was determined using a sample from the reaction. Reaction progress was monitored at regular intervals via the AN until an AN of < 0.5 mg of KOH per g sample was achieved. The batch was then cooled and the catalyst destroyed by addition of aqueous sodium hydroxide solution.

20 The reaction output from the esterification was transferred into a stirred flask fitted with a stirrer. The equipment was purged with nitrogen (6 l/h). Under vacuum (about 1 - 5 mbar), the reaction output was slowly heated and the temperature increased to 160°C. After complete distillation of the excess alcohol the product was cooled to 80°C and filtered. The filtrate was subjected to NMR
25 analysis to determine the composition of the ester radicals in the product.

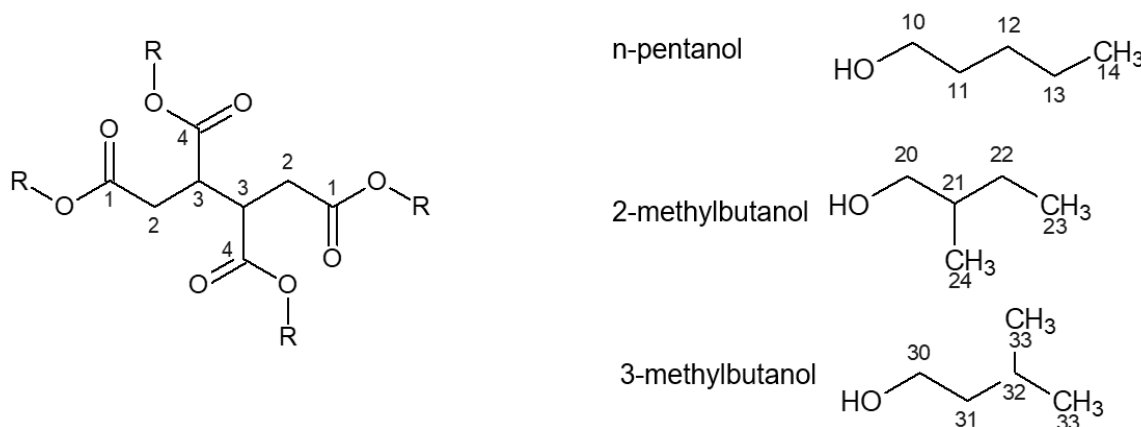
NMR analysis

The composition of the tetraisopentyl-1,2,3,4-butanetetracarboxylic esters, i.e. the respective
30 proportion of the different isomeric butyl radicals based on the entirety of all butyl radicals, may be determined for example by ^1H -NMR and ^{13}C -NMR spectroscopy. Due to its higher accuracy, determination of the composition was here performed using ^1H -NMR spectroscopy on a solution of the tetraisopentyl-1,2,3,4-butanetetracarboxylic ester mixtures in deuteriochloroform (CDCl_3). To record the ^1H -NMR spectra about 20 mg of substance were dissolved in about 0.6 ml of CDCl_3 (in
35 each case containing about 1% by mass of TMS) and filled into an NMR tube having a diameter of 5 mm. The CDCl_3 used was first dried over a molecular sieve to prevent corruption of the measured values by any water present.

The NMR spectroscopy analyses may in principle be carried out using any commercially available NMR instrument. For the present NMR spectroscopy analyses a Bruker Avance 500 instrument was used. The ^1H -NMR spectra were recorded at a temperature of 300 K with a delay of $d1 = 5$ seconds, 32 scans, a pulse length of about $12\ \mu\text{s}$ (30° excitation pulse) and a sweep width of 10 000 Hz with a 5 mm Prodigy Cryo sample head (CPPBO) with Bruker Cooling Unit (BCU 05). The resonance signals were recorded relative to the chemical shifts of tetramethylsilane (TMS = 0 ppm) as internal standard. Other commercial NMR instruments give comparable results with the same operating parameters.

Figure 1 below is merely to aid comprehension of the elucidated method of determination. Relevant here is the assigned numbering of the carbon atoms of the methyl groups and the methylene groups adjacent to the oxygen atom in each case in an n-pentyl radical (C_{14}H_3 and C_{10}H_2), in a 2-methylbutyl radical (C_{23}H_3 , C_{24}H_3 and C_{20}H_2) and in a 3-methylbutyl radical (C_{33}H_3 and C_{30}H_2).

Figure 1: Numbering of the carbon atoms in the different pentyl radicals



wherein each R= n-pentanol, 2-methylbutanol or 3-methylbutanol.

The obtained ^1H -NMR spectra of the mixtures of tetra-isopentyl-1,2,3,4-butanetetracarboxylic esters have resonance signals in the range from 0.8 ppm to 1.0 ppm which are formed by the signals of the hydrogen atoms of the methyl group(s) of the isomeric pentyl substituents (C_{14}H_3 , C_{23}H_3 , C_{24}H_3 , C_{33}H_3). The signals in the range of chemical shifts from 3.60 to 4.40 ppm may essentially be assigned to the hydrogen atoms of the methylene group adjacent to the oxygen in the alcohol radical (C_{10}H_2 , C_{20}H_2 , C_{30}H_2). The protons on C20 are subject to a high-field shift due to the adjacent tertiary carbon atom and appear between 4.03 and 3.84 ppm while the protons on C10 and C30 give signals at lower shifts of 4.20 to 4.03 ppm and are mutually overlapping.

Quantification was effected by comparative determination of the area under the respective resonance signals, i.e. the area enclosed by the signal from the baseline. Commercial NMR software has program functions for integration of the signal area. In the present NMR spectroscopy study, the integration was conducted with the aid of the software TopSpin®, Version 3.6.

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To determine the mean degree of branching of the isomeric pentyl radicals in the mixture according to the invention, the integral value of the signals in the range from 0.68 to 1.11 ppm ($I(\text{CH}_3)$) is first divided by the integral value of the signals in the range from 3.60 to 4.40 ppm ($I(\text{OCH}_2)$). In this way, an intensity ratio which indicates the ratio of the number of hydrogen atoms present in a methyl group to the number of hydrogen atoms present in a methylene group adjacent to an oxygen is obtained. Since three hydrogen atoms per methyl group and two hydrogen atoms in every methylene group adjacent to an oxygen are present, the intensities have to be divided by 3 and 2 respectively to obtain the ratio of the number of methyl groups to the number of methylene groups adjacent to an oxygen in the pentyl radical. Since a linear *n*-pentyl radical having only one methyl group and one methylene group adjacent to an oxygen does not contain any branching and accordingly has to have a degree of branching of 0, it is necessary to subtract the value 1 from the ratio.

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The mean degree of branching DB can thus be calculated by the formula

$$\text{DB} = 2/3 * I(\text{CH}_3)/I(\text{OCH}_2) - 1$$

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from the intensity ratio measured. In this formula, DB is the mean degree of branching, $I(\text{CH}_3)$ is the area integral assigned to the methyl hydrogen atoms, and $I(\text{OCH}_2)$ is the area integral of the methylene hydrogen atoms adjacent to the oxygen.

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The product may contain 2-methylbutyl radicals and 3-methylbutyl radicals each having a degree of branching of 1, and also *n*-pentyl radicals having a degree of branching of 0, which means that the maximum mean degree of branching of any tetraisopentyl ester is always 1. From the deviation of the mean degree of branching from the value of 1, it is therefore possible to determine the molar proportion of *n*-pentyl radicals (x_{pentyl}) in the molecule.

$$x_{\text{pentyl}} = 1 - \text{DB}$$

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The proportion of 2-methylbutyl radicals cannot be calculated using the integration of the baseline-separated signals in the range from 3.60 to 4.40 ppm.

Here too, the signals of the protons on C20 ($C^{20}H_2$; multiplet between 3.95 and 4.28 ppm) are separated from the signals of the protons on C10 and C30 ($C^{10}H_2$ and $C^{30}H_2$; multiplet between 4.29 and 4.55 ppm) in the minimum of the valley cut between the signal groups.

The molar proportion of 2-methylbutyl radicals ($x_{2\text{-methylbutyl}}$) can be calculated by the formula

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$$x_{2\text{-methylbutyl}} = I(OC^{19}H_2) / I(OCH_2)$$

by forming the ratio of the intensity of the signals for the $OC^{20}H_2$ protons ($I(OC^{20}H_2)$) to the intensity of all OCH_2 protons ($I(OCH_2)$).

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The molar proportion of 3-methylbutyl radicals ($x_{3\text{-methylbutyl}}$) is thus calculated from the difference between the two previous molar proportions and 1.

$$x_{3\text{-methylbutyl}} = 1 - x_{2\text{-methylbutyl}} - x_{\text{pentyl}}$$

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The aforementioned method made it possible to determine the proportions of the respective radicals in the samples (see table 1).

20 Table 1: Composition of the ester mixtures by NMR analysis

	Proportion of 2-methylbutyl (product) [%]	Proportion of 3-methylbutyl (product) [%]	Proportion of n-pentyl (product) [%]
Ex. 1*	8.3	0	91.7
Comp. Ex. 2	52.2	0	47.8
Comp. Ex. 3	59.5	0	40.5
Comp. Ex. 4	59.0	21.2	19.8
Comp. Ex. 5	45.3	0	54.7
Comp. Ex. 6	39.2	0	60.8
Comp. Ex. 7	32.5	33.4	34.1
Comp. Ex. 8	0	0	100
Comp. Ex. 9	100	0	0

*Inventive

The ester mixtures from table 1 were investigated in terms of application-relevant properties.

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1) Plastisol production

PVC plastisols, as used for manufacturing topcoat films for example, were produced. The amounts in the plastisol formulations are each reported in parts by mass (phr). The formulation is reported in table 2.

Table 2: Plastisol formulation

	phr
PVC (Vestolit P1430 K70 – Ultra; from Vestolit)	100
Plasticizer	50
Epoxidized soybean oil as co-stabilizer (Edenol D81, from Emery Oleochemicals)	3
Heat stabilizer based on Ba/Zn ((Reagens MBL 197/9PF, from Reagens)	2

First the liquid constituents and then the pulverulent constituents were weighed out into a PE beaker. The mixture was stirred manually with a spatula in such a way that no unwetted powder remained present. The mixing beaker was then clamped into the clamping means of a dissolver stirrer. After switching on the stirrer, the speed was slowly increased to about 2000 rpm (revolutions per minute). During that time, the plastisol was carefully deaerated. To this end, the pressure was adjusted to a pressure below 20 mbar. As soon as the plastisol had reached a temperature of about 30°C, the speed was lowered to about 350 rpm. Henceforth, the plastisol was deaerated at that speed and a pressure below 20 mbar for 9 minutes. This ensured that there could be no premature partial gelation during homogenizing of the plastisol.

1.1) Determination of plastisol viscosity

The viscosity of the plastisols produced in example 1) was measured with a Physica MCR 101 rheometer (from Anton Paar Germany GmbH) with the aid of the accompanying software, using the rotation mode and the CC27 measuring system. The measurement was conducted after the plastisols had been thermally equilibrated at 25°C for 24 hours after their production.

The measurement involved the following points:

- preliminary shear at 100 s^{-1} for a period of 60 seconds, during which no measurements were taken
- downward shear rate ramp from 200 s^{-1} to 0.1 s^{-1} . 30 measurement points were recorded, each with a measurement point duration of 10 seconds.

The measurements were conducted at room temperature. What was determined in each case was the viscosity obtained at a shear rate of 10 s^{-1} . The results of the viscosity measurements for the plastisols produced in example 1) with the plasticizers specified in each case are listed in table 3.

5 Table 3: Results of viscosity measurement

Sample	Viscosity at shear rate 10 s^{-1} [Pa*s]
Ex. 1*	3.85
Comp. Ex. 2	5.32
Comp. Ex. 3	5.67
Comp. Ex. 4	6.14
Comp. Ex. 5	5.07
Comp. Ex. 6	4.68
Comp. Ex. 7	5.01
Comp. Ex. 8	3.80
Comp. Ex. 9	8.27

It is apparent that the inventive mixture (sample 1) has a viscosity comparable to that of sample 8 (pure tetra-n-pentyl ester of 1,2,3,4-butanetetracarboxylic acid).

10 1.2) Gelation characteristics

The gelation characteristics of the plastisols from example 1) were examined using a Physica MCR 101 instrument (from Anton Paar) in oscillation mode with a parallel plate analysis system (PP25) operated under shear stress control. An additional temperature control hood was connected to the system in order to achieve the best possible heat distribution. The following measurement parameters were established:

Mode: Temperature gradient (linear temperature ramp)
 Start temperature: 25°C
 20 End temperature: 180°C
 Heating/cooling rate: 5 K/min
 Oscillation frequency: $4\text{--}0.1 \text{ Hz}$ ramp (logarithmic)
 Cycle frequency ω : 10 s^{-1}
 Number of measurement points: 63
 25 Measurement point duration: 0.5 min
 Automatic gap adjustment
 Constant measurement point duration
 Gap width 0.5 mm

Analysis procedure:

The spatula was used to apply a few drops of the plastisol to be analysed, free from air bubbles, to the lower plate of the analysis system. In so doing, it was ensured that, after the analysis system had been assembled, it was possible for some plastisol to exude uniformly out of the analysis system (not more than about 6 mm in any direction). The temperature control hood was subsequently positioned over the sample and the analysis was started. This involved determining the so-called complex viscosity of the plastisol as a function of temperature. Onset of gelation was apparent from a sudden sharp rise in complex viscosity. The earlier the onset of this rise in viscosity, the better the gelation capacity of the system. The measurement curves obtained were used to determine, by interpolation, the temperatures for each plastisol at which a complex viscosity of 1000 Pa*s was measured. The results are listed in table 4.

15

Table 4: Results of gelation rate measurement

Sample	Temperature at complex viscosity of 1000 s ⁻¹ [Pa*s]
Ex. 1*	80.3
Comp. Ex. 2	81.4
Comp. Ex. 3	82
Comp. Ex. 4	82.8
Comp. Ex. 5	81.3
Comp. Ex. 6	81.1
Comp. Ex. 7	82.8
Comp. Ex. 8	80.1
Comp. Ex. 9	82.9

It is apparent that the inventive mixture (sample 1) has a comparably low gelation rate to that of sample 8 (pure tetra-n-pentyl ester of 1,2,3,4-butanetetracarboxylic acid) and thus markedly lower than the other comparative examples.

2) Film production

The plastisols produced in example 1) were each processed into films of 1 mm in thickness.

For this purpose, first of all, high-gloss release paper (from Sappi, Italy) was trimmed to a size of 30 x 44 cm and inserted in the clamping frame of the LTSV coating installation for the Mathis oven. The clamping frame was subsequently placed onto the guide frame, the Mathis oven (model LTF) was adjusted to 200°C, and the frame was preheated once that temperature had been attained.

- 5 The coating bar was subsequently inserted into the clamping means and the coating bar gap was adjusted via preliminary experiments such that the film thickness on conclusion of gelation was 1 mm (+/- 0.05 mm). The plastisol was spread over the clamped release paper with the aid of the coating bar (speed 3 m/min). Thereafter, the coating bar was removed and the clamping frame was moved into the oven. After gelation (2 minutes at 200°C), the frame was moved back out of the oven and, after cooling, the film was removed from the paper.
- 10

2.1) Volatility of the plasticizers in the films

Three circles per sample were punched out of the PVC films produced in example 2) with a punch (circle; diameter: 5 cm). The samples were equilibrated in a desiccator for 16 hours.

- 15 The sample circles were weighed out on an analytical balance and introduced into a wire basket, and the latter was closed with a bulldog clip.

- 130 ml of activated carbon were introduced into a tin can (1 l, tall form). The first wire basket with sample was then placed onto the middle of the activated carbon, and a further 130 ml of activated carbon were applied to the sample circle. In total, the tin cans were thus filled layer by layer with 520 ml of activated carbon and 3 wire baskets with sample. Finally, a further upper layer of 130 ml of activated carbon was introduced.
- 20

- The perforated lid of the tin cans was placed onto the cans without pressure. The filled tin cans were positioned in a heating cabinet heated to 120°C in such a way that the ventilator in the cabinet was not closed and the cans were not in contact with one another. Air exchange and ventilation flap were each set at 10%. After 72 hours at 120°C, the samples were taken out of the cabinet again and cooled down, then the individual samples were taken out of the baskets, conditioned for another 16 hours in a desiccator and then reweighed on an analytical balance. The resultant difference in mass results from the loss of plasticizer. The average was formed from the three differences in mass in each case, and the percentage loss of plasticizer was calculated. The results are listed in table 5.
- 25
- 30

Table 5: Results of volatility measurement

Sample	Weight loss [%]
Ex. 1*	1.54
Comp. Ex. 2	1.95
Comp. Ex. 3	2.06
Comp. Ex. 4	1.96
Comp. Ex. 5	1.79
Comp. Ex. 6	1.74
Comp. Ex. 7	1.94
Comp. Ex. 8	1.56
Comp. Ex. 9	2.14

It is apparent that the inventive mixture (sample 1) has the lowest viscosity of all samples. Only sample 8 (pure tetra-n-pentyl ester of 1,2,3,4-butanetetracarboxylic acid) shows a comparably low volatility.

2.2) Glass transition temperature by DSC

For the measurement a small circle ($\varnothing$ 4.5 mm) was punched out of the PVC films produced according to example 2). This sample was analysed in an aluminium crucible (perforated crucible lid) under nitrogen with a Mettler Toledo DSC 1 using the following settings:

Dry nitrogen gas: about 45 ml (STP)/min (= standard ml per minute)
 Gas nitrogen (purge gas): about 180 ml (STP)/min
 Cooling: liquid nitrogen (auxiliary reservoir 1.5 bar)
 Method:
 [1] 25.0 to 120.0°C, 25.0 K/min
 [2] 120.0°C, 5.00 min isothermal
 [3] 120.0°C to -50.0°C, 25.0 K/min
 [4] -50.0 to -120.0°C, 10.0 K/min
 [5] -120.0°C, 3.00 min isothermal
 [6] -120 to 50.0°C, 10.0 K/min
 Synchronization switched on

The various temperature ramps eliminate the thermal history of the sample and therefore serve for higher reproducibility of the results. For the glass transition, the peak maximum of the first derivative from the ramp [6] was evaluated. The resultant heat flow was plotted as a function of the measurement temperature. The results are shown in table 6.

Table 6: Results of glass transition measurement

Sample	Peak maximum [°C]
Ex. 1*	-29.6
Comp. Ex. 2	-23.8
Comp. Ex. 3	-23.0
Comp. Ex. 4	-22.6
Comp. Ex. 5	-25.9
Comp. Ex. 6	-26.7
Comp. Ex. 7	-21.7
Comp. Ex. 8	-29.7
Comp. Ex. 9	-18.0

It is apparent that the inventive mixture (sample 1) has a comparably low peak maximum to that of sample 8 (pure tetra-n-pentyl ester of 1,2,3,4-butanetetracarboxylic acid).

Claims

1. Mixture of tetraisopentyl esters of 1,2,3,4-butanetetracarboxylic acid, wherein 6 to 12 mol% of the isopentyl radicals in the mixture are 2-methylbutyl radicals, 88 to 94 mol% of the isopentyl radicals in the mixture are n-pentyl radicals and 0 to 4 mol% of the isopentyl radicals in the mixture are 3-methylbutyl radicals.
2. Mixture according to Claim 1, wherein 6 to 10 mol% of the isopentyl radicals in the mixture are 2-methylbutyl radicals, 90 to 94 mol% of the isopentyl radicals in the mixture are n-pentyl radicals and 0 to 2 mol% of the isopentyl radicals in the mixture are 3-methylbutyl radicals.
3. Mixture according to Claim 1, wherein 7 to 9 mol% of the isopentyl radicals in the mixture are 2-methylbutyl radicals, 91 to 93 mol% of the isopentyl radicals in the mixture are n-pentyl radicals and 0 to 2 mol% of the isopentyl radicals in the mixture are 3-methylbutyl radicals.
4. Mixture according to any of Claims 1 to 3, wherein less than 1 mol% of the isopentyl radicals in the mixture are 3-methylbutyl radicals.
5. Mixture according to Claim 4, wherein less than 0.5 mol% of the isopentyl radicals in the mixture are 3-methylbutyl radicals.
6. Process for producing the mixture of tetraisopentyl esters of 1,2,3,4-butanetetracarboxylic acid according to any of Claims 1 to 5, wherein the producing is carried out either by esterification of 1,2,3,4-butanetetracarboxylic acid with an isopentanol mixture or by transesterification of the tetramethyl ester of 1,2,3,4-butanetetracarboxylic acid with an isopentanol mixture.
7. Process according to Claim 6, wherein the water of reaction formed during the esterification is separated during the reaction.
8. Process according to Claim 6 or 7, wherein the esterification is performed at a temperature in the range from 120°C to 250°C.
9. Use of the mixture of tetraisopentyl esters of 1,2,3,4-butanetetracarboxylic acid according to any of Claims 1 to 5 as a plasticizer for polymers, in particular for PVC or vinyl chloride-containing copolymers.
10. Plasticizer composition containing the mixture of tetraisopentyl esters of 1,2,3,4-butanetetracarboxylic acid according to any of Claims 1 to 5 and at least one further plasticizing compound.

11. Plasticizer composition according to Claim 10, wherein the further plasticizing compound is selected from the group consisting of adipates, benzoates, for example monobenzoates or glycol dibenzoates, chlorinated hydrocarbons (so-called chloroparaffins), citrates, cyclohexanedicarboxylates, epoxidized fatty acid esters, epoxidized vegetable oils, epoxidized acylated glycerides, furandicarboxylates, phosphates, succinates, sulfonamides, sulfonates, terephthalates, trimellitates and oligomeric or polymeric esters based on adipic acid, succinic acid or sebacic acid.
12. Plasticizer composition according to Claim 10 or 11, wherein the plasticizer composition contains less than 5% by weight, more preferably less than 0.5% by weight, particularly preferably less than 0.1% by weight, of phthalates.
13. Plastics composition containing the mixture of tetraisopentyl esters of 1,2,3,4-butanetetracarboxylic acid according to any of Claims 1 to 5 or the plasticizer composition according to any of Claims 10 to 12 and one or more polymers.
14. Plastics composition according to Claim 13, wherein the one or more polymers are selected from the group consisting of PVC, homo- or copolymers based on ethylene, propylene, butadiene, vinyl acetate, glycidyl acrylate, glycidyl methacrylate, ethyl acrylate, butyl acrylate or methacrylate with alkoxy radicals of branched or unbranched alcohols having one to ten carbon atom(s), acrylonitrile or cyclic olefins, polyvinylidene chloride (PVDC), polyacrylates, in particular polymethyl methacrylate (PMMA), polyalkyl methacrylate (PAMA), polyureas, silylated polymers, fluoropolymers, especially polyvinylidene fluoride (PVDF), polytetrafluoroethylene (PTFE), polyvinyl acetate (PVAc), polyvinyl alcohol (PVA), polyvinyl acetals, especially polyvinyl butyral (PVB), polystyrene polymers, especially polystyrene (PS), expandable polystyrene (EPS), acrylonitrile-styrene-acrylate (ASA), styrene-acrylonitrile (SAN), acrylonitrile-butadiene-styrene (ABS), styrene-maleic anhydride copolymer (SMA), styrene-methacrylic acid copolymer, polyolefins, especially polyethylene (PE) or polypropylene (PP), thermoplastic polyolefins (TPO), polyethylene-vinyl acetate (EVA), polycarbonates, polyethylene terephthalate (PET), polybutylene terephthalate (PBT), polyoxymethylene (POM), polyamide (PA), polyethylene glycol (PEG), polyurethane (PU), thermoplastic polyurethane (TPU), polysulfides (PSu), biopolymers, especially polylactic acid (PLA), polyhydroxybutyral (PHB), polyhydroxyvaleric acid (PHV), polyesters, starch, cellulose and cellulose derivatives, especially nitrocellulose (NC), ethylcellulose (EC), cellulose acetate (CA), cellulose acetate/butyrate (CAB), rubber and silicones.
15. Use of the plastics composition according to Claim 13 or 14 in adhesives, sealing compositions, coating compositions, lacquers, paints, plastisols, foams, synthetic leathers,

floor coverings (for example the topcoat), roofing membranes, underbody protection, fabric coatings, cables, wire insulation, hoses, extruded articles, films, in the field of automotive interiors, in wallpapers, inks, toys, contact sheets, foodstuffs packaging or medical articles, for example tubes or blood bags.