

Stabilization of diesters of dicarbonic acid

The present invention relates to the use of phosphorus compounds as stabilizers of diesters of dicarbonic acid, mixtures containing diesters of dicarbonic acid and phosphorus compounds, and also the use of these mixtures for preserving foods and materials.

- 5 Diesters of dicarbonic acid are used, inter alia, for preserving foods, in particular drinks, as components of antimicrobial reagents, for deactivating enzymes in fermentation processes, or for the synthesis of fine chemicals or polymers. Diesters of dicarbonic acid are used, in addition, for example as catalysts for the oxidation of amines, or for synthesis, for example in the introduction of protecting groups.
- 10 It is known that the stability of diesters of dicarbonic acid can be relatively low at room temperature, and in particular at elevated temperature. In particular during purification, for example in purification by distillation, or during relatively long storage, decomposition of diesters of dicarbonic acid can therefore occur. This decomposition can impair the quality and purity of the diesters of dicarbonic acid. In addition, the decomposition generally
- 15 proceeds the more rapidly the more impurities are present. High purity and stabilization of diesters of dicarbonic acid are therefore highly desirable.

Methods for improving the thermal stability of diesters of dicarbonic acid are already known from the prior art. For instance, it is proposed, for example, to stabilize dialkyl pyrocarbonates by adding metal sulphates (cf. JP-A 48-4016). A disadvantage of this

20 method, however, is that these metal sulphates are sparingly to poorly miscible with the diesters of dicarbonic acid.

In addition, it is known to stabilize diesters of dicarbonic acid by adding boron compounds (cf. JP-A 46-37810). However, a disadvantage in this case is the toxicity of the corresponding boron compounds. Usage in foods does not come into consideration for these

25 additions.

In addition, carbonyl compounds and also heteroanalogous carbonyl compounds have been proposed as additives increasing the storage stability of solutions of diesters of dicarbonic acid in solvents inert to diesters of dicarbonic acid (cf. DE-A 3231397). However, solutions of diesters of dicarbonic acid in customary aprotic solvents scarcely come into consideration

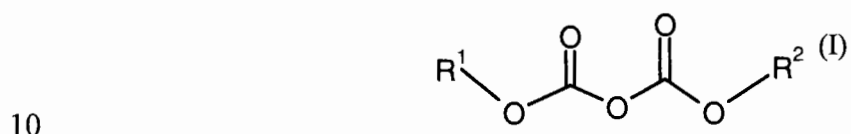
30 as an addition to foods. In addition, stabilizing effects may only be achieved using relatively high percentage amounts of additions.

There was therefore a requirement for stabilizers which are suitable for protecting diesters of dicarbonic acid effectively against thermal breakdown.

Surprisingly, it has now been found that diesters of dicarbonic acid can be stabilized by addition of phosphorus compounds against thermal and/or chemical breakdown reactions
 5 such as can occur, for example in storage or purification such as purification by distillation.

The present invention therefore relates to the use of at least one phosphorus compound for stabilization of diesters of dicarbonic acid against chemical and/or thermal breakdown reactions.

The diesters of dicarbonic acid are preferably compounds of the general formula (I)



where

R^1 and R^2 independently of one another are straight-chain or branched C_1 - C_8 -alkyl, cycloalkyl, C_2 - C_8 -alkenyl, C_2 - C_8 -alkynyl or benzyl,
 15 each of which is optionally monosubstituted to polysubstituted, identically or differently by halogen; nitro; cyano; C_1 - C_6 -alkoxy; dialkylamino; or are phenyl which is optionally monosubstituted to polysubstituted, identically or differently by halogen; nitro; cyano; alkyl; haloalkyl; alkoxy; haloalkoxy; acyl; acyloxy; alkoxycarbonyl; carboxyl,

preferably

20 R^1 and R^2 independently of one another are straight-chain or branched C_1 - C_8 -alkyl, C_2 - C_8 -alkenyl or benzyl,

particularly preferably

R^1 and R^2 independently of one another are straight-chain or branched C_1 - C_5 -alkyl, C_3 -alkenyl or benzyl,

25 and very particularly preferably

R^1 and R^2 independently of one another are methyl, ethyl, isopropyl, tert-butyl, tert-amyl, allyl or benzyl.

The stabilizers are phosphorus compounds, preferably compounds of phosphorus with oxygen, more preferably containing at least one phosphorus-oxygen bond, particularly preferably compounds from the series of phosphorus oxides and phosphorus-oxygen acids and derivatives thereof.

- 5 Those which may be mentioned as phosphorus-oxygen acids by way of example are: ortho and meta acids of the general formulae H_3PO_n and HPO_{n-1} where $n = 2, 3, 4$ and 5 , diacids of the general formula $H_4P_2O_n$ where $n = 4, 5, 6, 7$ and 8 , and also polyphosphoric acids of the general formula $H_{n+2}P_nO_{3n+1}$ where $n = 3-15\ 000$.

- 10 As derivatives of the phosphorus-oxygen acids, those which may be mentioned are, in particular, salts and esters thereof. As examples of esters, those which may be mentioned are mono-, di- and trialkyl esters, mono-, di- and trialkenyl esters, mono-, di- and triaryl esters and also esters with sugar derivatives or glycerol derivatives. The alkyl radicals in the said mono-, di- and trialkyl esters are, for example, methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, tert-butyl radicals. The esters can also be present as salts, for example alkali metal
15 or alkaline earth metal salts, such as sodium, potassium, magnesium or calcium salts.

- As further derivatives of the phosphorus-oxygen acids, mention may be made of compounds which in addition contain at least one phosphorus-carbon bond. Examples of phosphorus-carbon-containing compounds of this type are derivatives of phosphonic acids, phosphonous acids or phosphinic acids and esters thereof. Examples of esters which may be mentioned are
20 mono-, di- and trialkyl esters, mono-, di- and trialkenyl esters, mono-, di- and triaryl esters and also esters with sugar derivatives or glycerol derivatives. The alkyl radicals in the said mono-, di- and trialkyl esters are, for example, methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, tert-butyl radicals. The esters can likewise be present as salts, for example alkali metal or alkaline earth metal salts such as sodium, potassium, magnesium or calcium salts.

- 25 As phosphorus compounds, very particular preference is given to phosphorus pentoxide (P_2O_5), hypophosphorous acid (H_3PO_2), phosphorous acid (H_3PO_3), aqueous or crystalline phosphoric acid (H_3PO_4), pyrophosphoric acid, metaphosphoric acid, polyphosphoric acids, dimethyl phosphate, trimethyl phosphate, phosphates such as sodium hydrogen phosphates or ammonium hydrogen phosphates, oleylphosphate, phytic acid, phosphorylcholine,
30 adenosine 3'-monophosphoric acid, 2-phosphonobutane-1,2,4-tricarboxylic acid, amino-trismethylenephosphonic acid, diethylenetriaminepentamethylenephosphonic acid or phosphonic-acid-group-containing ion exchangers, such as, for example disclosed by WO 2000001458 or by EP-A 355007.

The phosphorus compounds can be used as pure substances or as aqueous or alcoholic solutions. The compounds can equally be dissolved in advance in pyrocarbonates or other suitable solvents. The phosphorus compounds can also be immobilized on surfaces, for example glass surfaces.

- 5 In addition, of course, use can be made of the different reactive phosphorus-halogen compounds which even in the presence of only small amounts of water hydrolyse, *in situ*, to give the abovementioned phosphorus compounds. Examples of these are phosphorus trichloride or phosphoryl chloride.

- 10 The the said stabilizers are generally used in an amount of 0.01 to 100 000 ppm, preferably in an amount of 0.1 to 10 000 ppm, particularly preferably in an amount of 0.1 to 3000 ppm, very particularly preferably in an amount of 0.1 to 2000 ppm, based on the diesters of dicarbonic acid or mixture thereof.

- 15 As a result of the use according to the invention, it is possible to stabilize diesters of dicarbonic acid in general against thermal and chemical breakdown reactions. Such breakdown reactions occur, for example, in storage.

The diesters of dicarbonic acid stabilized according to the invention are distinguished by improved storage stability. For instance, the diesters of dicarbonic acid stabilized in this manner can be stored for a plurality of months at room temperature without decomposition of the diesters of dicarbonic acid being observed.

- 20 The present invention further relates to mixtures containing one or more diesters of dicarbonic acid of the formula (I) illustrated above and one or more of the above generally and preferably described phosphorus compounds generally in an amount of 0.01 to 100 000 ppm, preferably in an amount of 0.1 to 10 000 ppm, particularly preferably in an amount of 0.1 to 3000 ppm, very particularly preferably in an amount of 0.1 to 2000 ppm,
25 based on the diesters of dicarbonic acid or mixture thereof. Very particular preference is given to mixtures of at least one diester of dicarbonic acid of the formula (I), in particular dimethyl dicarbonate and/or diethyl dicarbonate with one or more phosphorus compounds from the series P_2O_5 , H_3PO_2 , H_3PO_3 , aqueous or crystalline H_3PO_4 , pyrophosphoric acid, metaphosphoric acid, polyphosphoric acids, dimethyl phosphate, trimethyl phosphate,
30 phosphates such as sodium hydrogen phosphates or ammonium hydrogen phosphates, oleyl phosphate, phytic acid, phosphorylcholine, adenosine 3'-monophosphoric acid, 2-phosphonobutane-1,2,4-tricarboxylic acid, aminotrismethylenephosphonic acid, diethylenetriaminepentamethylenephosphonic acid, phosphorus trichloride, phosphoryl chloride or phosphonic-acid-group-containing ion exchangers.

The inventive mixtures can be stored over a period of a plurality of months without decomposition of the diesters of dicarbonic acid present therein occurring.

The inventive mixtures are outstandingly suitable for preserving foods and in particular drinks against infection and/or decomposition by microorganisms, such as, for example,
5 bacteria, fungi or yeasts.

The present invention likewise relates to the use of the inventive mixtures for preservation of foods and drinks.

The diesters of dicarbonic acid stabilized according to the invention are outstandingly suitable, for example, as cold disinfectants for still or carbonated drinks such as soft drinks,
10 vitamin drinks, fruit juice drinks, tea drinks, alcoholic or dealcoholized wine drinks, fruit punches or some beers. Customarily, for this the diesters of dicarbonic acid are added in amounts between 10 and 250 ppm close in time to packaging the drinks. Admixture to the drinks is performed using special metering pumps. The diesters of dicarbonic acid act so as to control a series of microorganisms such as fermentative yeasts, moulds or fermentative
15 bacteria. Examples which may be mentioned here are for instance *Saccharomyces cerevisiae*, *Mycoderma*, *Brettanomyces* spp, *Lactobacillus brevis*, *Lactobacillus buchneri* and many others.

Thermal breakdown reactions of diesters of dicarbonic acid also occur, furthermore, in particular in the workup or distillation of diesters of dicarbonic acid as carried out, for
20 example, in the context of the production method for diesters of dicarbonic acid. By means of the inventive use of phosphorus compounds it is possible to distil diesters of dicarbonic acid with relatively low losses and in relatively high purity.

The present invention therefore further relates to a method for the purification by distillation of diesters of dicarbonic acid, by admixing one or more diesters of dicarbonic acid of the
25 above-specified formula (I) with one or more of the above generally and preferably described phosphorus compounds, generally in an amount of 0.01 to 100 000 ppm, preferably in an amount of 0.1 to 10 000 ppm, in each case based on the diesters of dicarbonic acid or mixture thereof, and subsequently distilling the mixture at a pressure of 5 to 100 mbar, preferably 10-70 mbar, and a temperature between 30 and 120°C, preferably
30 between 40 and 90°C. Distillation columns customary in industry come into consideration for the distillation.

The yields of diesters of dicarbonic acid in the distillation are customarily >99%.

The examples hereinafter are intended to illustrate the subject matter of the invention without, however, restricting it thereto.

Example 1

Corresponding to the data in Tables 1-6, in each case defined amounts of a defined high-purity diester of dicarbonic acid and the respectively stated additions were weighed in a 10 ml round-bottomed flask equipped with a magnetic stirrer. The exact amounts of the
5 additions used in each case are likewise given in the tables.

The round-bottomed flask was tightly closed by a septum. In this septum was situated an orifice in which a Teflon tube was attached, which was passed into a vertical silicone-oil-filled 50 ml burette calibrated to 0.1 ml. On the scale of the burette, the amount of the carbon dioxide developing as a result of the decomposition of the diester of dicarbonic acid could be
10 read off. The flask was promptly lowered into a constant temperature oil bath (stirred at 500 rpm) as specified in Tables 1-6 for the respective experiment. The depth of immersion of the flask was 2.0 cm.

After the respectively stated time, generally after 1, 2, 5, 10 and 15 minutes, the gas volume was read off. The gas volume is an index of the degree of decomposition of the diesters of
15 dicarbonic acid to give CO₂. It thus inversely reflects the degree of stabilization by the additions tested.

In most cases the experiments were repeated in order to ensure reproducibility. Meaningful reproducibility was present in each case.

The results may be taken from the tables. High-purity pyrocarbonate, in the observed time,
20 released little carbon dioxide, but even contact with small amounts of silica gel, manganese dioxide or else only rough surfaces such as scratched glass drastically accelerated decomposition. Small amounts of the stabilizers were sufficient for effective reduction of the decomposition.

The fewer gaseous decomposition products diesters of dicarbonic acid release under
25 temperature stress, the more favourably does distillation under vacuum proceed.

Table 1**Diethyl dicarbonate, 5000 ppm addition of stabilizer**

Temperature [°C]	130	130	130	130	130	130	130
Diethyl dicarbonate Amount [g]	1	1	1	1	1	1	1
Addition	without	silica gel	silica gel	silica gel	silica gel	silica gel	silica gel
Amount [mg]		10	10	10	10	10	10
Addition of stabilizer	without	without	$\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$	crystalline H_3PO_4	85% strength H_3PO_4	sodium sulphite	Na 4- hydroxy- benzoate
Amount [mg]			5	5	5	5	5
Gas evolution [ml]							
Minute 1	0.5	2.5	1.7	1.5	1.8	3.0	1.0
Minute 2	1.0	7.2	4.9	3.9	3.4	8.9	3.7
Minute 5	1.2	28.9	13.6	8.6	7.5	29.5	19.0
Minute 10	1.3	46.3	18.4	10.0	10.8	46.7	35.0
Minute 15	1.3	50.0	21.2	12.4	13.0	50.0	48.5

Table 2**Dimethyl dicarbonate, 20 000 ppm addition of stabilizer**

Temperature [°C]	100	100	100	100
Dimethyl dicarbonate Amount [g]	1	1	1	1
Addition	without	silica gel	silica gel	silica gel
Amount [mg]		10	10	10
Addition of stabilizer	without	without	crystalline H ₃ PO ₄	85% strength H ₃ PO ₄
Amount [mg]			20	20
Gas evolution [ml]				
Minute 1	0.5	1.3	0.7	0.1
Minute 2	1.4	3.9	1.7	0.3
Minute 5	3.3	20.1	4.5	2.3
Minute 10	5.7	49.0	10.8	9.6
Minute 15	8.8	50.0	16.7	14.4

Table 3

Dimethyl dicarbonate, 1670 ppm addition of stabilizer

Temperature [°C]	100	100	100	100	100	100	100	100	100	100
Dimethyl dicarbonate Amount [g]	3	3	3	3	3	3	3	3	3	3
Addition	without	silica gel	silica gel	silica gel	silica gel	silica gel	silica gel	silica gel	silica gel	silica gel
Amount [mg]	10	10	10	10	10	10	10	10	10	10
Addition of stabilizer	without	without	water	boric acid	$\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$	crystalline H_3PO_4	85% strength H_3PO_4	B_2O_3	phytic acid	
Amount [mg]		5	5	5	5	5	5	5	5	5
Gas evolution [ml]										
Minute 1	0.1	1.0	2.4	0.2	1.5	0.1	0.1	0.4	1.7	
Minute 2	0.2	3.4	8.0	1.4	5.5	0.2	0.4	2.1	4.7	
Minute 5	0.6	20.3	26.8	7.8	31.5	0.9	0.9	9.8	11.0	
Minute 10	0.8	46.1	50.0	18.5	40.6	1.5	1.2	22.6	16.3	
Minute 15	1.3	50.0	50.0	34.1	50.0	2.3	1.6	32.9	19.9	

Temperature [°C]	100	100	100	100	100	100	100	100	100	100
Dimethyl dicarbonate Amount [g]	3	3	3	3	3	3	3	3	3	3
Addition	silica gel	silica gel	silica gel	silica gel	silica gel	silica gel	silica gel	silica gel	silica gel	silica gel
Amount [mg]	10	10	10	10	10	10	10	10	10	10
Addition of stabilizer	phosphorus pentoxide	NaH ₂ PO ₄ · H ₂ O	disodium hydrogen phosphate	Ca-phosphoryl-choline chloride · 4H ₂ O	2-phosphono-butane-1,2,4-tricarboxylic acid Na ₂ salt	2-phosphono-butane-1,2,4-tricarboxylic acid in H ₂ O 50% diester mixture)	oleyl phosphate and diammonium hydrogenphosphate	Phosphorous acid + pyrophosphoric acid		
Amount [mg]	5	5	5	5	5	5	5	5	2.5 + 2.5	
Gas evolution [ml]										
Minute 1	1.1	1.4	0.5	0.9	1.0	0.9	1.4	0.9	0.2	
Minute 2	3.1	4.4	1.9	3.2	3.5	3.2	3.7	3.2	0.5	
Minute 5	4.9	18.2	12.4	16.7	12.1	6.9	9.7	12.6	1.3	
Minute 10	5.7			30.3	28.8	7.9	15.0	26.1	2.0	
Minute 15	6.1			40.3	45.1	9.5	19.1	36.2	3.2	

Temperature [°C] Dimethyl dicarbonate Amount[g]	100 3	100 3	100 3	100 3	100 3	100 3	100 3	100 3
Addition Amount [mg]	silica gel 10	silica gel 10	silica gel 10	silica gel 10	silica gel 10	silica gel 10	silica gel 10	silica gel 10
Addition of stabilizer Amount [mg]	dimethyl phosphate 5	trimethyl phosphate 5	pyrophosphoric acid 5	phosphorous acid 5	H ₃ PO ₂ in H ₂ O 50% 5	aminotris- methylene- phosphonic acid in H ₂ O 50% 5	diethylenetriamine- pentamethylene- phosphonic acid in H ₂ O 15% 5	PCl ₃ 5
Gas evolution [ml] Minute 1 Minute 2 Minute 5 Minute 10 Minute 15	0.2 0.9 2.4	0.3 1.4 8.0	0.3 1.0 1.6	0.3 0.9 2.0	0.1 0.3 1.2	1.2 4.3 10.8	0.6 1.5 2.6	0.9 1.9 2.8 3.5 4.3

Table 4

Dimethyl dicarbonate, 1670 ppm addition of stabilizer

Temperature [°C]	100	100	100	100	100	100	100	100	100
Dimethyl dicarbonate Amount [g]	3	3	3	3	3	3	3	3	3
Addition	manganese dioxide manganese dioxide manganese dioxide manganese dioxide manganese dioxide manganese dioxide manganese dioxide manganese dioxide								manganese dioxide
Amount [mg]	10	10	10	10	10	10	10	10	10
Addition of stabilizer	without								2-phosphono-butane-1,2,4-tricarboxylic acid in H ₂ O 50% and HCl 15% water
Amount [mg]	5	5	5	5	5	5	5	5	5
Gas evolution [ml]									
Minute 1	0.1	3.8	0.2	1.0	0.6	1.4	1.5	7.1	
Minute 2	0.2	9.3	0.8	2.1	1.5	3.9	3.1	26.4	
Minute 5	0.6	21.7	1.4	3.9	2.5	8.2	6.8	35.4	
Minute 10	0.8	31.1	1.8	5.4	2.9	11.4	9.7	46.1	
Minute 15	1.3	41.5	2.3	6.4	3.4	12.9	12.1	50.0	

Table 5**Dimethyl dicarbonate, 1670 ppm addition of stabilizer**

Temperature [°C]	100	100	100
Dimethyl dicarbonate Amount [g]	3	3	3
Addition	without	surface of the flask highly internally scratched	surface of the flask highly internally scratched
Addition of stabilizer	without	without	85% strength H ₃ PO ₄
Amount [mg]			5
Gas evolution [ml]			
Minute 1	0.1	4.0	1.7
Minute 2	0.2	6.0	2.6
Minute 5	0.6	7.6	3.4
Minute 10	0.8	10.0	4.8
Minute 15	1.3	11.0	5.5

Table 6**Dimethyl dicarbonate, <1000 ppm addition of stabilizer**

Temperature [°C]	100	100	100	100
Dimethyl dicarbonate Amount [g]	3	3	3	3
Addition	silica gel	silica gel	silica gel	silica gel
Amount [mg]	10	10	10	10
Addition of stabilizer	5 ppm 85% strength H ₃ PO ₄	10 ppm 85% strength H ₃ PO ₄	50 ppm 85% strength H ₃ PO ₄	100 ppm 85% strength H ₃ PO ₄
Gas evolution [ml]				
Minute 1	1.5	0.7	1.1	1.3
Minute 2	4.0	1.9	2.2	2.6
Minute 5	14.3	6.8	5.3	4.9
Minute 10	32.2	25.0	8.2	6.5
Minute 15		39.9	10.9	7.1

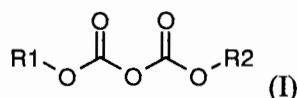
Example 2

Dimethyl dicarbonate was stored at room temperature. As an index of decomposition, the dimethyl carbonate content was determined by GC. Without addition of a stabilizer composition, the dimethyl carbonate content of the sample was 1090 ppm after 3 months.

The experiment was repeated, but approximately 5 ppm of phosphoric acid were added. The experimental series was carried out using 10 different samples. The dimethyl carbonate content in this case after 3 months was on average only 210 ppm.

Claims

1. Use of at least one compound from the series of phosphorus compounds for stabilization of diesters of dicarbonic acid against chemical and thermal breakdown reactions.
- 5 2. Use according to Claim 1, characterized in that the phosphorus compounds are compounds of phosphorus with oxygen which contain at least one phosphorus-oxygen bond.
3. Use according to at least one of Claims 1 and 2, characterized in that the phosphorus compounds are those from the series of phosphorus oxides and phosphorus-oxygen acids and derivatives thereof.
- 10 4. Use according to Claim 3, characterized in that the phosphorus-oxygen acids are ortho and meta acids of the general formulae H_3PO_n and HPO_{n-1} where $n = 2, 3, 4$ and 5, diacids of the general formula $H_4P_2O_n$ where $n = 4, 5, 6, 7$ and 8, and also polyphosphoric acids of the general formula $H_{n+2}P_nO_{3n+1}$ where $n = 3-15\ 000$.
- 15 5. Use according to at least one of Claims 1 to 4, characterized in that the diesters of dicarbonic acid are compounds of the general formula



where

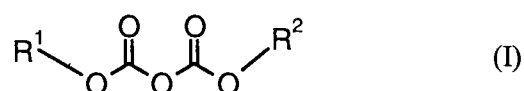
- 20 R^1 and R^2 independently of one another are straight-chain or branched C_1 - C_8 -alkyl, cycloalkyl, C_2 - C_8 -alkenyl, C_2 - C_8 -alkynyl or benzyl,

each of which is optionally monosubstituted to polysubstituted, identically or differently by halogen; nitro; cyano; C_1 - C_6 -alkoxy; dialkylamino; or are phenyl which is optionally monosubstituted to polysubstituted, identically or differently by halogen; nitro; cyano; alkyl; haloalkyl; alkoxy; haloalkoxy; acyl; acyloxy; alkoxy-carbonyl; carboxyl.

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6. Use according to at least one of Claims 1 to 5, characterized in that the diesters of dicarbonic acid are dimethyl dicarbonate or diethyl dicarbonate.

7. Use according to at least one of Claims 1 to 6, characterized in that the phosphorus compounds are used in an amount of 0.01 to 100 000 ppm, based on diesters of dicarbonic acid or mixture thereof.
8. Use according to at least one of Claims 1 to 7, characterized in that the stabilization against breakdown reactions is during workup, extraction, distillation or storage.
9. Mixtures containing one or more diesters of dicarbonic acid of the general formula



where

- R^1 and R^2 independently of one another are straight-chain or branched C_1 - C_8 -alkyl, cycloalkyl, C_2 - C_8 -alkenyl, C_2 - C_8 -alkynyl or benzyl, each of which is optionally monosubstituted to polysubstituted, identically or differently by halogen; nitro; cyano; C_1 - C_6 -alkoxy; dialkylamino; or are phenyl which is optionally monosubstituted to polysubstituted, identically or differently by halogen; nitro; cyano; alkyl; haloalkyl; alkoxy; haloalkoxy; acyl; acyloxy; alkoxycarbonyl; carboxyl,

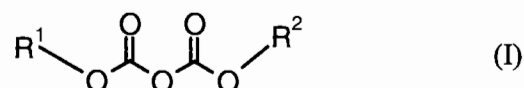
and one or more phosphorus compounds in an amount of 0.01 to 100 000 ppm, based on diesters of dicarbonic acid or mixture thereof.

10. Mixture according to Claim 9, characterized in that the phosphorus compounds are compounds of phosphorus with oxygen which contain at least one phosphorus-oxygen bond.
11. Mixture according to at least one of Claims 9 and 10, characterized in that the phosphorus compounds are those from the series of phosphorus oxides and phosphorus-oxygen acids and derivatives thereof.
12. Mixture according to at least one of Claims 9 to 11, characterized in that it contains at least one compound from the series dimethyl dicarbonate and diethyl dicarbonate and at least one phosphorus compound from the series P_2O_5 , H_3PO_2 , H_3PO_3 , aqueous or crystalline H_3PO_4 , pyrophosphoric acid, metaphosphoric acid, polyphosphoric acids, dimethyl phosphate, trimethyl phosphate, phosphates such as sodium hydrogen phosphates or ammonium hydrogen phosphates, oleyl phosphate, phytic

acid, phosphorylcholine, adenosine 3'-monophosphoric acid, 2-phosphonobutane-1,2,4-tricarboxylic acid, aminotrimethylenephosphonic acid, diethylenetriaminepentamethylenephosphonic acid, phosphorus trichloride, phosphoryl chloride or phosphonic-acid-group-containing ion exchangers.

- 5 13. Use of a mixture according to at least one of Claims 9 to 12 for preservation of foods, drinks and materials.

14. Method for the purification by distillation of diesters of dicarboxylic acid, characterized in that one or more diesters of dicarboxylic acid of the general formula



- 10 where

- R¹ and R² independently of one another are straight-chain or branched C₁-C₈-alkyl, cycloalkyl, C₂-C₈-alkenyl, C₂-C₈-alkynyl or benzyl, each of which is optionally monosubstituted to polysubstituted, identically or differently by halogen; nitro; cyano; C₁-C₆-alkoxy; dialkylamino; or are phenyl which is optionally monosubstituted to polysubstituted, identically or differently by halogen; nitro; cyano; alkyl; haloalkyl; alkoxy; haloalkoxy; acyl; acyloxy; alkoxy-carbonyl; carboxyl,
- 15

is admixed with one or more phosphorus compounds and the mixture is subsequently distilled.

- 20 15. Method according to Claim 14, characterized in that the phosphorus compounds are compounds of phosphorus with oxygen which contain at least one phosphorus-oxygen bond.

16. Method according to at least one of Claims 14 and 15, characterized in that the phosphorus compounds are those from the series of phosphorus oxides and phosphorus-oxygen acids and derivatives thereof.
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17. Method according to at least one of Claims 14 to 16, characterized in that use is made of one or more phosphorus compounds in an amount of 0.01 to 100 000 ppm, based on diesters of dicarboxylic acid or mixture thereof.

18. Method according to at least one of Claims 14 to 17, characterized in that distillation is performed at a pressure of 5 to 100 mbar and a temperature between 30 and 120°C.