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(54) **Title:** PROCESS FOR PURIFYING ALKYLATED PHENOLS

(57) **Abstract:** In a process for purifying a reaction mixture containing, in addition to a desired alkylphenol compound from the group of 2-(tert-butyl)phenol, 3-(tert-butyl)phenol, 4-(tert-butyl)phenol, 2,4-di(tert-butyl)phenol, 2,6-di(tert-butyl)phenol, 3,5-di(tert-butyl)phenol or 2,4,6-tri(tert-butyl)phenol, at least one further alkylphenol compound from the same or another group of alkylphenols, the desired compound is first separated as a distillate fraction from a less volatile mixture or residue. The distillate fraction is then subjected to a crystallization, preferably a fractional layer crystallization, in which the distillate fraction is cooled and the desired alkylphenol compound is crystallized out. The undesired compounds are enriched in the mother liquor in this process and can be separated off. High-purity alkylphenol compounds having a low colour index can be obtained by this purification process on a large industrial scale.

Process for purifying alkylated phenols

The present invention relates to a process for purifying alkylated phenols by means of distillation and subsequent crystallization.

It is known that the various processes for preparing alkylated phenols yield a mixture of differently substituted phenols that then have to be worked up. In principle, distillation is suitable as a process for separating the reaction mixture. However, the mixtures often contain a plurality of isomers having very similar boiling points, with the result that distillative separation is not possible or only possible at high cost. A further problem in distillative purification, in particular the purification of polyalkylated phenols having a correspondingly high molecular weight is the high melting point of the compounds since high-melting compounds readily result in blockage of the separating column.

A process for purifying alkylated phenols, in particular 2,4,6-tri(tert-butyl)phenol is described in WO 00/14043. In this process, the reaction mixture containing the desired 2,4,6-tri(tert-butyl)phenol is first subjected to a vacuum distillation. The vacuum distillation yields a distillate containing more volatile compounds and a residue that contains the desired 2,4,6-tri(tert-butyl)phenol and at least one other, undesired alkylated phenol compound. The residue is then subjected to a melt crystallization in order to produce the 2,4,6-tri(tert-butyl)phenol having a purity of > 99%.

The process taught by WO 00/14043 has the advantage that the desired alkylated phenol compound is not distilled, but only low boilingcompounds are separated as distillate from the residue containing the desired compound. This avoids the above mentioned problems in the distillative purification of alkylated phenol compounds having high molecular weight. A further advantage of the process is that high purities are said to be achievable. However, there continues to be a need in industry for very pure alkylated, in particular colourless phenolic compounds. It is also desirable that the purification process can be performed inexpensively, continuously and on a large scale.

The object of the present invention is therefore to provide an improved process by which a desired alkylated phenolic compound that is either 2-(tert-butyl)phenol, 3-(tert-butyl)phenol, 4-(tert-butyl)phenol, 2,4-di(tert-butyl)phenol, 2,6-di(tert-butyl)phenol, 3,5-di(tert-butyl)phenol or 2,4,6-tri(tert-butyl)phenol can be separated from a reaction mixture containing various alkylated phenolic compounds and can be made available in high purity, preferably greater than 99.5%. The object is, in particular, to make available 4-(tert-butyl)phenol from a mixture containing at least one further compound having a similar boiling point, in particular an alkylated phenolic compound, and to make it available in high purity. A further object is to propose a purification process that does not need any solvents for the purification. The crystallization should also be capable of being performed without adduct formation. An object is also to propose a process with which compounds having a purity of > 99.5 and, preferably, > 99.9% can be obtained inexpensively and on a large industrial scale. Furthermore, the purified compounds should have low colour index.

According to the invention, the object is achieved in that the desired compound being either 2-(tert-butyl)phenol, 3-(tert-butyl)phenol, 4-(tert-butyl)phenol, 2,4-di(tert-butyl)phenol, 2,6-di(tert-butyl)phenol, 3,5-di(tert-butyl)phenol or 2,4,6-tri(tert-butyl)phenol is first separated from less volatile components or component mixture as a distillate, and the distillate is then subjected to a crystallization, in which the distillate (stream or fraction) is cooled and the desired alkylphenol compound is crystallized and separated from the undesirable compounds being enriched in the mother liquor. Surprisingly, the desired compound can be obtained in still higher purity than by the process described in WO 00/14043 if subjected to distillation prior to crystallization. In contrast to the teaching of WO 00/14043, it was found that a distillative separation of the desired compound is possible. Surprisingly, the result of the subsequent crystallization is even better if the desired compound is first distilled off as a distillate fraction and then crystallized. The reason for this appears to be that the high boilers contained in the residue, markedly reduce the separation efficiency of the subsequent crystallization. This is the case in the process of WO 00/14043. This impairs the efficiency of the separation process, and higher costs are also incurred. In addition, the shape of the crystals of the crystallized, desired compound may be altered unfavourably by the high boilers present in the distillation residue, with the result that the separation of the mother liquor after crystallization and also after sweating is made more difficult. This is of importance if the final product shall have a purity of > 99.0%, preferably > 99.5%, and very particularly preferably of > 99.9%.

Advantageously, the relevant distillate fraction is subjected to an essentially solvent-free melt crystallization. As a result of dispensing with additional solvents, the process is environmentally friendly and easy to perform. In accordance with a particularly preferred process variant, the melt crystallization is a layer crystallization according to the dynamic, e.g. falling-film, or static principle or a combination of the two processes. Crystals of high purity can be obtained by means of the above mentioned crystallization processes. However, it is also conceivable to perform a suspension crystallization instead of the above mentioned processes. High purities and yields can be achieved by all these crystallization purification processes in conjunction with a distillative pre-purification of the distillate fraction.

Expediently, during the distillation, a plurality of distillate fractions are branched off, of which a first distillate predominantly contains compounds that are more volatile than the desired compound, and at least one further, e.g. second distillate (stream or fraction) contains the desired compound in a high proportion by weight. The second distillate containing the desired compound can be removed as side stream or as head stream of a distillation column. It is also conceivable to use more than one distillation column.

Expediently, the reflux of the distillation column used for the distillation is adjusted in such a way that the proportion by weight of the desired compound in the distillate is > 90%, preferably > 95% and very particularly preferably > 99%. As a result of the high proportion of the desired product in the distillate stream fed to the crystallization process, the crystallization process can be performed faster, more efficiently and with higher yield. It is also of importance, in particular, that the distillate containing the main product is substantially freed of high boilers.

Advantageously, a fractional melt crystallization of the falling-film type is used, in which process the distillate containing the desired alkylphenol compound is allowed to flow down over one side of a wall or cooling surface as a surface film and the other side of the wall is cooled with a coolant to such an extent that the desired alkylphenol compound crystallizes out on the wall and forms a crystal layer. The use of the falling-film type melt crystallization has the advantage that high purities can be achieved and the crystallization process is rapid. Instead of dynamic layer crystallization, however, static layer crystallization may be used. In the case of static layer crystallization, the distillate is conveyed into a crystallization container where it is contacted as liquid (melt)by one side of a cooled wall without forced movement (convection). Expediently, both in the case of static layer crystallization and in the case of dynamic layer crystallization, the mixture is cooled until the proportion of the desired compound in the mixture has decreased to such a value that a further crystallization is of low productivity, whereupon the mixture depleted of the desired alkylphenol compound is discharged as residue. Both in the case of static and of dynamic layer crystallization, the wall serving as cooling surface may be designed as vertically disposed tube(s) or a flat wall(s), preferably disposed vertically, that is hollow and can have a coolant flowing through it. The cooled walls may have the form of flat, ribbed or curved plates or of smooth or ribbed tubes.

Advantageously, to obtain the desired alkylphenol compound, the crystal layer is melted fractionally and at least one sweating phase and also a crystal phase containing the desired alkylphenol compound of high purity is obtained. Preferably, the sweating phase is fed back to the crystallization, in particular in a subsequent crystallization cycle. The sweating phase of a certain crystallization cycle can be temporarily stored in a container and the contents of said container can be added to the distillate fraction fed to a subsequent crystallization cycle. Such a procedure has the advantage that the total yield of the desired compound can be increased.

It is conceivable to perform a suspension crystallization in which the distillate containing the desired alkylphenol compound is brought into contact with one side of a cooled wall and the other side of the wall is cooled with a coolant to such an extent that crystal nuclei are produced on the cooled wall that contain the enriched, desired compound and the crystal nuclei thus produced are scraped off the cooled wall by means of a scraping device and are transferred to a suspension stream and remain suspended in the melt, respectively. The suspension stream containing the scraped-off crystal nuclei can then be fed into a washing column or into a cascade comprising a plurality of washing columns in which the suspension stream is divided into at least two fractions, of which at least one fraction contains the highly purified desired compound. In another variant of the process, the suspension stream can be conveyed from the scratching device into a container fitted with a stirring mechanism or with another stirring device or into a cascade of such containers, where it is divided into at least two said fractions. However, a type of suspension crystallization may also be used in which the distillate stream containing the desired alkylphenol compound is fed directly into a washing column or into a cascade comprising a plurality of washing columns in which the distillate flow is divided into at least two fractions, of which at least one fraction contains the highly purified desired compound.

The desired compound to be purified and obtained can be one of the compounds named hereafter: 2-(tert-butyl)phenol, 3-(tert-butyl)phenol, 4-(tert-butyl)phenol, 2,4-di(tert-butyl)phenol, 2,6-di(tert-butyl)phenol, 3,5-di(tert-butyl)phenol or 2,4,6-tri(tert-butyl)phenol. It is present together with further compounds, which may likewise originate from the group comprising the abovementioned compounds. In general, the product mixture to be purified is a product accruing in the alkylation of phenols. The literature discloses a multiplicity of processes that describe the production of alkylphenols by alkylation of phenols, cresols or xylenols. As a rule, a mixture of various alkylphenol isomers is produced in these alkylation reactions. Correspondingly, the undesired compounds to be removed from the mixture are, for example, phenols, cresols, xylenols, isobutene, phenyl ethers, for example tert-butyl phenol ether, isomers of the desired compound and more highly alkylated compounds of the desired compound. The composition of the mixture accruing during the alkylation may be influenced, in particular, by the choice of the educts, the catalyst, the quantitative ratio of the educts, temperature, pressure and duration of the reaction.

Compounds that can be purified by the process according to the invention preferably have a boiling point of greater than 80°C, preferably greater than 150°C and very particularly preferably, greater than 180°C under normal conditions. It has been found that particularly pure end products can be obtained from reaction mixtures containing high-boiling components, in particular isomer mixtures of 2 or more alkylated phenols, by a preliminary distillation of the reaction mixture in which the desired compound is separated as a distillate fraction and subsequent crystallization, in particular fractional melt crystallization, of the particular distillate fraction. Expediently, the distillation is performed at reduced pressure. Vacuum distillation can reduce the boiling point of high-boiling organic compounds to such an extent that the danger of blocking of the distillation column is low.

The present invention also relates to the use of a device comprising

- a distillation column having an inlet for the mixture to be purified, a first outlet provided at the foot of the column for draining off the distillation residue and at least a second outlet at the head of the column for draining off the distillate; and
- a crystallization device having at least one inlet and one outlet; and also
- lines for connecting the outlet of the distillation column to the inlet of the crystallization device and also, optionally, intermediate containers or intermediate tanks for the temporary storage of the distillate fractions originating from the distillation;

for purifying a mixture containing, in addition to a desired alkylphenol compound that is either 2-(tert-butyl)phenol, 3-(tert-butyl)phenol, 4-(tert-butyl)phenol, 2,4-di(tert-butyl)phenol, 2,6-di(tert-butyl)phenol, 3,5-di(tert-butyl)phenol or 2,4,6-tri(tert-butyl)phenol, at least a further differently substituted alkylphenol compound. Further advantageous variants of use are defined in the sub-claims.

The invention is explained in greater detail below by way of example with reference to the figures. In the figures:

Figure 1	shows a diagrammatic view of a first exemplary embodiment of a purifying device for purifying alkylated phenols using a distillation column and a crystallization device;
Figure 2	shows another example of the embodiment of the purifying device in which additionally a storage vessel for the intermediate storage of the distillate fraction is comprised;
Figure 3	shows diagrammatically the individual product flow through the purifying device in accordance with Figure 1;
Figure 4	shows diagrammatically the individual product flow through a purifying device comprising more than one distillation column.

The exemplary embodiment 11 in accordance with Figure 1 for purifying alkylated phenols comprises a distillation column 13 and a crystallization device 15. The distillation column 13 has an inlet 17 on the jacket 19 of the distillation column for feeding in a mixture to be separated, a first outlet 21 at the head 23 of the column 13 for removing a first distillate stream, an outlet 25 on the jacket 23 of the column 13 for removing a second distillate stream or side stream and a third outlet 27 at the foot 29 of the column 13 for removing a distillation residue. A feed line 31 serves to supply a mixture to be purified to the inlet 17. Furthermore, a line 33 is connected to the outlet 27 in order to convey the distillation sump product to a container (not shown in this figure) or to a device for further processing.

The distillation column 13 has a known structure, not shown in greater detail, in order to achieve the separation effect necessary for separating a mixture. The column may be filled, for example, in a known way with structured packings (for example, EP-A-1 153 639, EP-A-1 145 761, EP-A-1 078 684, EP-A-1 022 057) or with packings such as, for example, Raschig or Nutter rings (for example, EP-A-0 176 174) or may be provided with plates (for example, WO 0124 901, US 5,360,583). The contents of the above mentioned documents are hereby incorporated by reference in the present description.

The crystallization device 15 has a container 35 having at least a first inlet 37 on the container for feeding in a mixture to be separated/purified, and at least a first outlet 41 at the bottom 43 of the crystallization device 15 for discharging a liquid phase situated at the bottom of the container. The outlet 41 is connected by means of a connecting line 45 to preferably two or more containers 47, 49. Valves 51, 53 make it possible to convey liquid originating from the crystallization container 35 optionally to the container 47 or 49. It is conceivable to provide a plurality of containers for the temporary storage of fractions originating from the crystallization purification process.

A re-circulation line 55 connects the collection chamber 57 provided at the lower end of the crystallization device 15 to the head 39 of the crystallization device. A pump 59 is provided in the re-circulation line 55 in order to deliver liquid from the bottom 43 to the head 39 of the crystallization device.

A return line 61 connects the container 47 to the crystallizer 15. Pump 63 provided in the return line 61 serves to deliver re-purified product temporarily stored in the first container 47 to the crystallizer. It is, however, conceivable to dispose the container 47 and, optionally, 49 above the crystallization device. In that case, the contents of the container can flow under the action of gravity into the container 35. Accordingly, a pump has to be provided in order to pump the contents of the crystallizer 35 into the tank 47 and the connecting line between the tank 47 and the crystallizer 35 must be capable of being shut off by means of a shutoff valve.

The outlet 25 of the distillation column 13 is connected to the crystallizer 15 via a line 65. A side stream from the distillation can be conveyed via the line 65 into the crystallizer 15. Advantageously, the distillate is collected in one or more buffer containers or buffer tanks and is temporarily stored.

The purification process is described more detailed below by reference to the installation in accordance with Figure 1. A mixture to be purified, which may be a crude product or an already pre-purified mixture, is fed via the feed line 13 and the inlet 17 to the distillation column 13. The bottom is heated until the mixture boils and the streams of the readily volatile constituents can be drawn off through the outlet 21 at the head of the column. Less volatile components, including also the desired compound, can be removed as a side stream from the distillation column. Again less volatile (non boiling) constituents are drawn off as residue via the line 33 and fed to a disposal or further processing system.

The side stream containing the desired product is conveyed into the crystallizer 15, optionally indirectly via buffer containers or buffer tanks. In accordance with a preferred variant of the process, the crystallizer 15 is a falling-film crystallizer, such as is described, for example, in US 3,621,664 (Saxer). The contents of the abovementioned patent are herewith to be incorporated by reference in the present application. Such falling-film crystallizers are obtainable from Sulzer Chemtech AG, Switzerland. In such a falling-film crystallizer, the mixture to be purified, in our case the side flow of the upstream distillation, is conveyed via the vertical cooling surfaces that are disposed in the container 35 and whose rear side is cooled by means of coolant that flows past. The temperature of the coolant is reduced below the melting point of the compound to be purified until the latter begins to crystallize out as a crystal layer on the cooling surfaces. The liquid mixture to be purified is circulated in the falling-film crystallizer and conveyed as a trickling-film or falling-film over the cooling surfaces or the crystal layer adhering to the crystal surfaces until the liquid mixture is depleted of the desired compound. The remaining mixture (mother liquor) is then conveyed as a residue to a container and, if further working-up is unproductive, disposed of as waste or fed back to the distillation or to the process units upstream of the distillation.

In the next step, the temperature of the coolant is slowly increased until the crystals deposited on the cooling surfaces begin to sweat. In the sweating phase, the temperature of the coolant is set to a suitable value below or directly at the melting point, normally between 0 and 15°C below the melting point of the compound to be purified, or is slowly increased to the vicinity of the melting point of the compound to be purified. The sweating fraction separated in this process is collected as one or more sub-fractions and, for example, temporarily stored in a container 47. If the sweating fraction is divided into two sweating sub-fractions, the first sub-fraction can be added, for example, to the mother liquor and the second sub-fraction to the feedstock (distillate). If "radiation sweating" or "gas sweating" (by contacting the crystal layer with a warmed gas) is used instead of sweating by increasing the temperature of the coolant, the temperature of the medium should be set higher than the melting point of the crystallized compound.

After sweating, the temperature is increased to the melting point or above it and the crystal layer is melted. The crystal fraction can then be conveyed as a pure product into the container 47 and fed to a subsequent use.

The above-mentioned process steps together form a crystallization cycle. The sweating phase or second sweating fraction originating from said crystallization cycle can be added to the distillate fraction, to be purified, of a subsequent crystallization cycle and the process can be repeated. It is conceivable to subject certain fractions yet again to a crystallization cycle in order to obtain high-purity end products and/or to increase the total yield.

It is conceivable to use a static crystallizer instead of a falling-film crystallizer, as is shown in Figure 2. In Figure 2, identical parts are denoted by the same reference numerals as in Figure 1. One difference in the crystallization device is that the container 35 is separated from the crystallizer 15. In addition, the pump 59 is used only for loading the static crystallizer.

Figure 3 illustrates the product flows in the purification of a reaction mixture in an installation in accordance with Figure 1. An optionally pre-treated reaction mixture 67 is conveyed to the distillation column 13 and separated into at least one head stream 69 predominantly containing more volatile compounds, a product stream 71 containing a high proportion of the desired compound and a residue 73. The product stream 71 is then separated in one or more crystallizers 15 into at least one residue 75 and a purified product 71a.

The product streams of Figure 4 differ from those of Figure 3 in that only the more volatile compounds are distilled off in a first distillation column 13 and the desired compound is fed, together with the less volatile compounds, as a stream 71 + 73 to a second distillation column 13a in which the stream 71 + 73 is separated into the product stream 71 that contains the desired compound in a high proportion and a residue 73 predominantly containing higher-boiling components.

Embodiments:

A reaction mixture originating from the preparation of 4-(tert-butyl)phenol was first distillatively prepurified and then crystallized and fractionated in a static crystallizer without adding solvent.

Example 1:

		Purity (wt%)
Feed:	62.4 kg	89.88
Mother liquor	19.4 kg	77.56
Sweating fraction	17.8 kg	91.16
Crystals	24.8 kg	98.5

Example 2:

A distillatively prepurified reaction mixture was used.

		Purity (wt%)
Feed:	47.90 kg	98.92
Mother liquor	10.43 kg	97.19
Sweating fraction	10.16 kg	98.12
Crystals	26.1 kg	99.91

Table 1 below shows the initial composition of a mixture to be purified which accrued in phenylalkylation using aluminium triphosphate as catalyst:

Component	**Proportion (wt%)**
Phenol	0.6
2-(tert-butyl)phenol	1.7
4-(tert-butyl)phenol	0.2
2,6-di(tert-butyl)phenol	75.9
2,4-di(tert-butyl)phenol	0.9
or 2,4,6-tri(tert-butyl)phenol	19.4

Table 1

Table 2 shows the composition of a mixture to be purified by the alkylation reaction (column 1) and after a transalkylation reaction (column 2). A cation exchanger resin was used as catalyst.

Component	**Proportion (wt%)**
Isobutene	0.19
Phenol	30.17
2-(tert-butyl)phenol	10.19
4-(tert-butyl)phenol	33.92
2,4-di(tert-butyl)phenol	23.71
2,4,6-tri(tert-butyl)phenol	0.41

Table 2

In a process for purifying a reaction mixture containing, in addition to a desired alkylphenol compound from the group of 2-(tert-butyl)phenol, 3-(tert-butyl)phenol, 4-(tert-butyl)phenol, 2,4-di(tert-butyl)phenol, 2,6-di(tert-butyl)phenol, 3,5-di(tert-butyl)phenol or 2,4,6-tri(tert-butyl)phenol, at least one further alkylphenol compound from the same or another group of alkylphenols, the desired compound is first separated as a distillate fraction from a less volatile mixture or residue. The distillate fraction is then subjected to a crystallization, preferably a fractional layer crystallization, in which the distillate fraction is cooled and the desired alkylphenol compound is crystallized out. The undesired compounds are enriched in the mother liquor in this process and can be separated off.

Key:

11	Embodiment, example
13	Distillation column
15	Crystallization device
17	Inlet
19	Jacket
21	First outlet at the head of the column
23	Head of the distillation column
25	Second outlet at the foot/bottom of the column
27	Third outlet at the foot/bottom of the column
29	Head of the distillation column
31	Feed line to the inlet 17
33	Line at the outlet 27
35	Container of the crystallization device
37	Inlet at container head
39	Container head
41	Outlet
43	Base
45	Connecting line
47, 49	Containers for receiving fractions
51, 53	Valves
55	Recirculation line
57	Collection chamber, collecting vessel
59	Pump
61	Return line
63	Pump
65	transfer line from distillation to crystallization
67	Raw reaction mixture
69	Head stream of the distillation
71, 71a	Product flow
73	Residue of the distillation
75	Residue of the crystallization

Claims

1. Process for purifying a mixture containing, in addition to a desired alkylphenol compound, at least one further alkylphenol compound, differently substituted than the desired alkylphenol compound, by means of distillation and subsequent crystallization, characterized in that the desired compound is either 2-(tert-butyl)phenol, 3-(tert-butyl)phenol, 4-(tert-butyl)phenol, 2,4-di(tert-butyl)phenol, 2,6-di(tert-butyl)phenol, 3,5-di(tert-butyl)phenol or 2,4,6-tri(tert-butyl)phenol and at least the desired compound is first separated by means of distillation from a less volatile compound as a distillate, and the distillate is then subjected to a crystallization, in which crystallization, the distillate is cooled and the desired alkylphenol compound is crystallized and the undesirable compounds, enriched in the mother liquor, are separated from the desired compound present as crystals.

2. Process according to Claim 1, characterized in that the distillate is subjected to a melt crystallization without adding solvent.

3. Process according to Claim 2, characterized in that the melt crystallization is a layer crystallization according to the dynamic principle, for example falling film, or static principle, or a combination of the two processes.

4. Process according to any one of Claims 1 to 3, characterized in that the melt crystallization is a suspension crystallization.

5. Process according to any one of Claims 1 to 3, characterized in that a fractional melt crystallization of the falling-film type is used, in which process the distillate containing the desired alkylphenol compound is

allowed to flow down on one side of a wall as a surface film and the other side of the wall is cooled with a coolant to such an extent that the desired alkylphenol compound crystallizes out on the wall and forms a crystal layer.

6. Process according to any one of Claims 1 to 3, characterized in that a static fractional melt crystallization is used, in which process the distillate containing the desired alkylphenol compound is brought into contact with one side of a cooled wall and the other side of the wall is cooled with a coolant to such an extent that the desired alkylphenol compound crystallizes out on the wall and forms a crystal layer.

7. Process according to Claim 5 or 6, characterized in that preferably vertically disposed tubes or a preferably vertically disposed flat wall are/is used as the wall serving as cooling surface.

8. Process according to any one of Claims 5 to 7, characterized in that the at least one cooled wall has the form of flat or curved plates or of smooth or ribbed (finned) tubes.

9. Process according to any one of Claims 1 to 8, characterized in that, to obtain the desired alkylphenol compound, the crystal layer is fractionally melted and at least one sweating phase and also a crystal phase containing the desired alkylphenol compound of high purity are obtained.

10. Process according to Claim 9, characterized in that the sweating phase is fed entirely or partly back to the crystallization.

11. Process according to Claim 9 or 10, characterized in that the sweating phase is temporarily stored in a container and the contents of the container are fed to at least one subsequent crystallization cycle.

12. Process according to any one of Claims 1 to 4, characterized in that a suspension crystallization is used, in which process the distillate containing the desired alkylphenol compound is brought into contact with one side of a cooled wall and the other side of the wall is cooled with a coolant to such an extent that there are produced on the cooled wall crystal nuclei that contain the enriched desired compound and the crystal nuclei produced in this way are scraped off the cooled wall by means of a scraping device and remain suspended in the melt.

13. Process according to Claim 12, characterized in that the suspension stream containing the scraped-off crystal nuclei is fed into a washing column or into a cascade comprising a plurality of washing columns in which the suspension is divided into at least two fractions of which at least one fraction contains the purified desired compound.

14. Process according to Claim 12 or 13, characterized in that the suspension stream containing the scraped-off crystal nuclei is fed into a stirred-tank cascade operating in countercurrent in which it is divided into at least two fractions of which at least one contains the highly purified desired compound or a mother liquor to be removed from the crystallization process.

15. Process according to Claim 12 or 13, characterized in that a suspension crystallization is used, in which process the distillate containing the desired alkylphenol compound is fed directly into a washing column or

into a cascade comprising a plurality of washing columns in which it is divided into at least two fractions of which at least one fraction contains the highly purified desired compound.

16. Process according to any one of Claims 1 to 15, characterized in that, during the distillation, a plurality of distillate streams or distillate fractions are branched off, of which at least a first distillate fraction essentially contains compounds that are more volatile than the desired compound, and a further e.g. second distillate fraction contains the desired compound in a high proportion by weight.

17. Process according to any one of Claims 1 to 16, characterized in that the reflux of the distillation column used in the distillation is adjusted so that the proportion by weight of the desired compound in a particular distillate stream is > 90%, preferably > 95% and, very particularly preferably, > 99%.

18. Process according to any one of Claims 1 to 17, characterized in that the liquid mixture in the crystallizer used is cooled until the proportion of the desired compound in the mixture has decreased to a value such that a further crystallization is of low productivity, whereupon the mixture depleted in regard to the desired alkylphenol compound is removed as residue.

19. Process according to any one of Claims 1 to 18, characterized in that the desired compounds have, under normal conditions, a melting point greater than 80°C, preferably greater than 150°C, and very particularly preferably, greater than 180°C.

20. Process according to any one of Claims 1 to 19, characterized in that the distillation is performed at reduced pressure.

21. The use of a device comprising
    - a distillation column having an inlet for a mixture to be purified, a first outlet provided at the foot of the column for draining off a distillation residue and at least a second outlet at the head of the column for for discharge of a distillatestream; and
    - a crystallization device having at least one inlet and one outlet; and also
    - lines for connecting the outlet of the distillation column to the inlet of the crystallization device and also, optionally, intermediate containers or intermediate tanks for the temporary storage of the distillate (fractions) originating from the distillation;

    for purifying a mixture containing, in addition to a desired alkylphenol compound that is either 2-(tert-butyl)phenol, 3-(tert-butyl)phenol, 4-(tert-butyl)phenol, 2,4-di(tert-butyl)phenol, 2,6-di(tert-butyl)phenol, 3,5-di(tert-butyl)phenol or 2,4,6-tri(tert-butyl)phenol, at least a further differently substituted alkylphenol compound.

22. Use according to Claim 21 and any one of Claims 1 to 20.

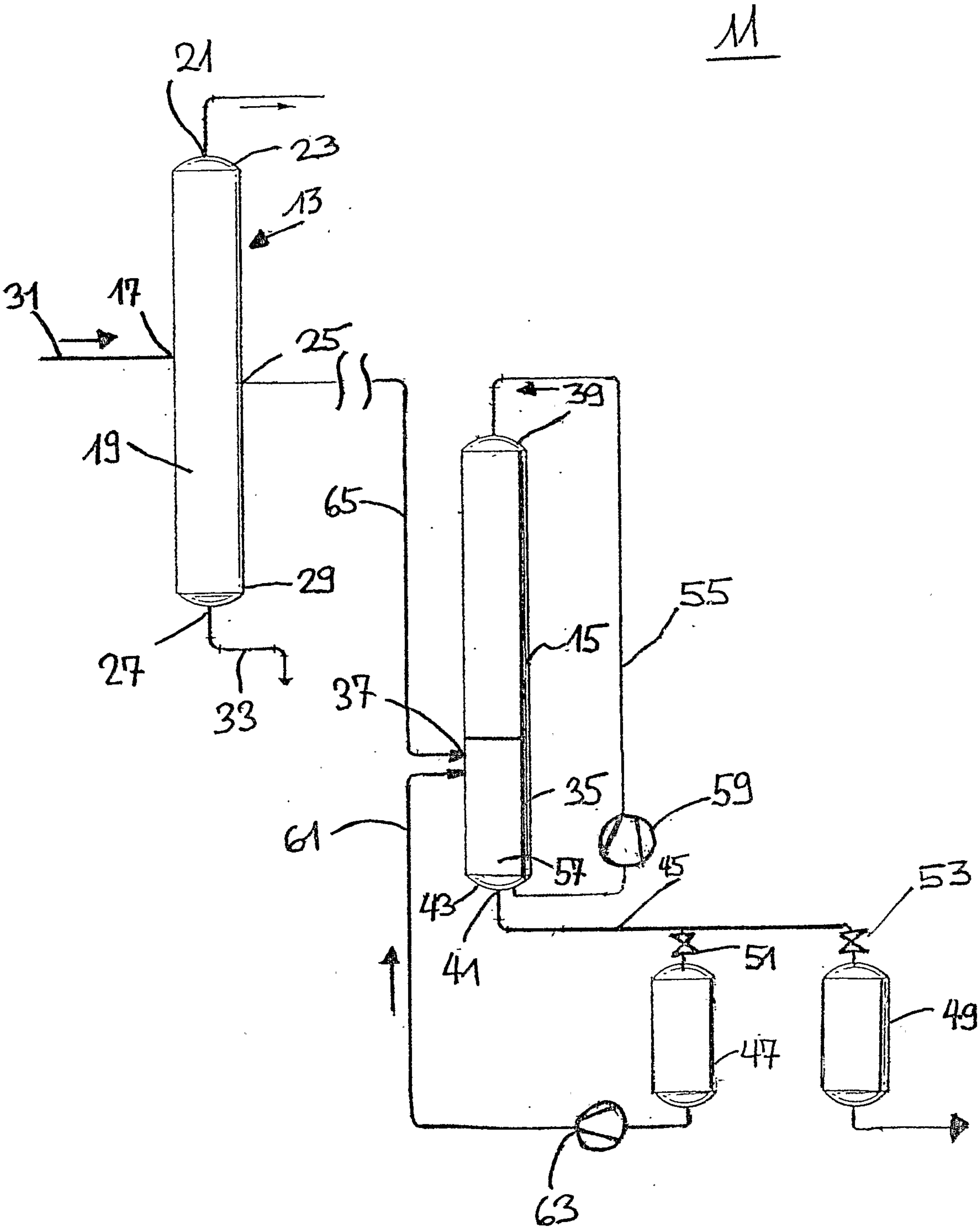
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Fig. 1

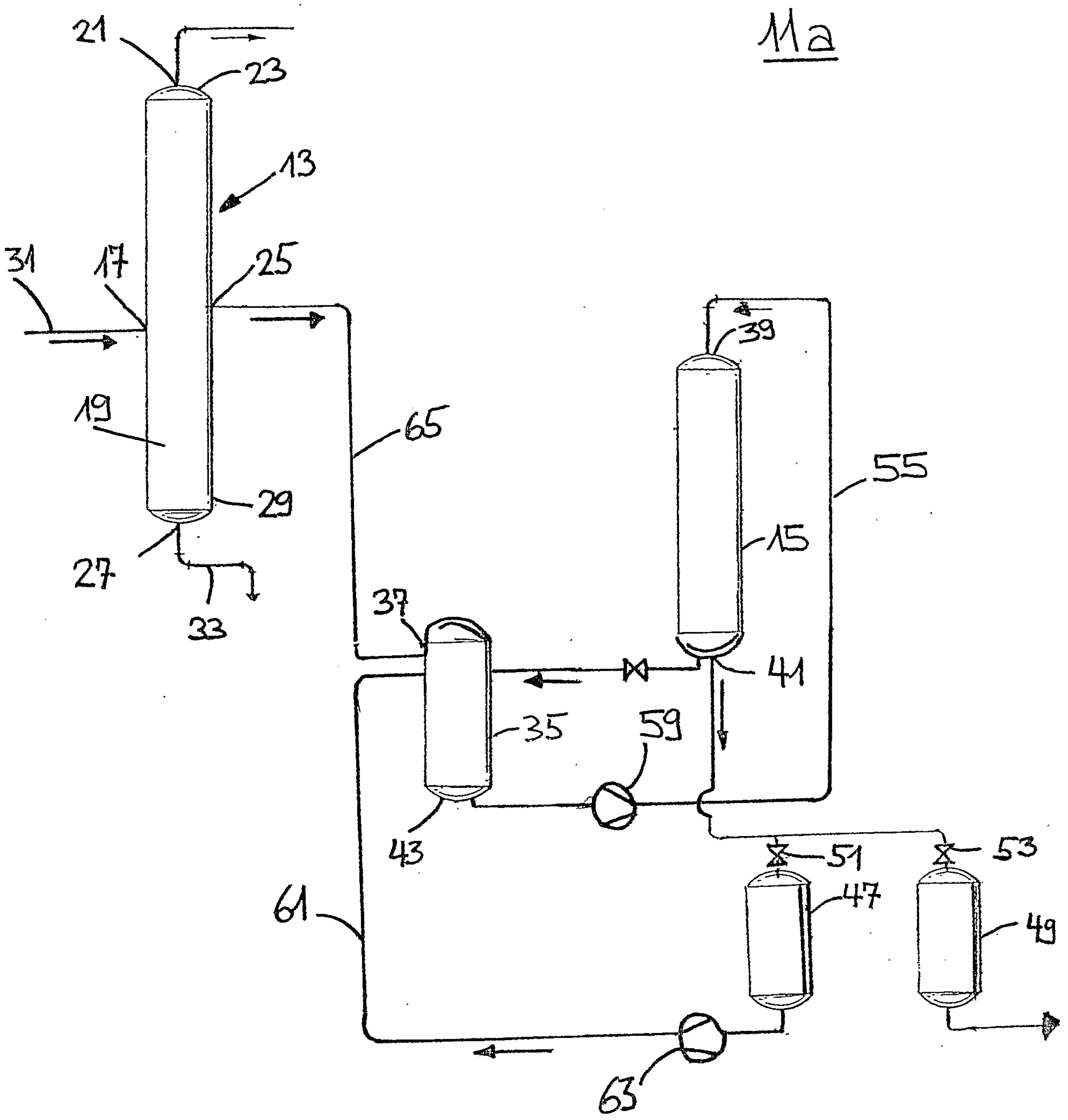
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Fig. 2

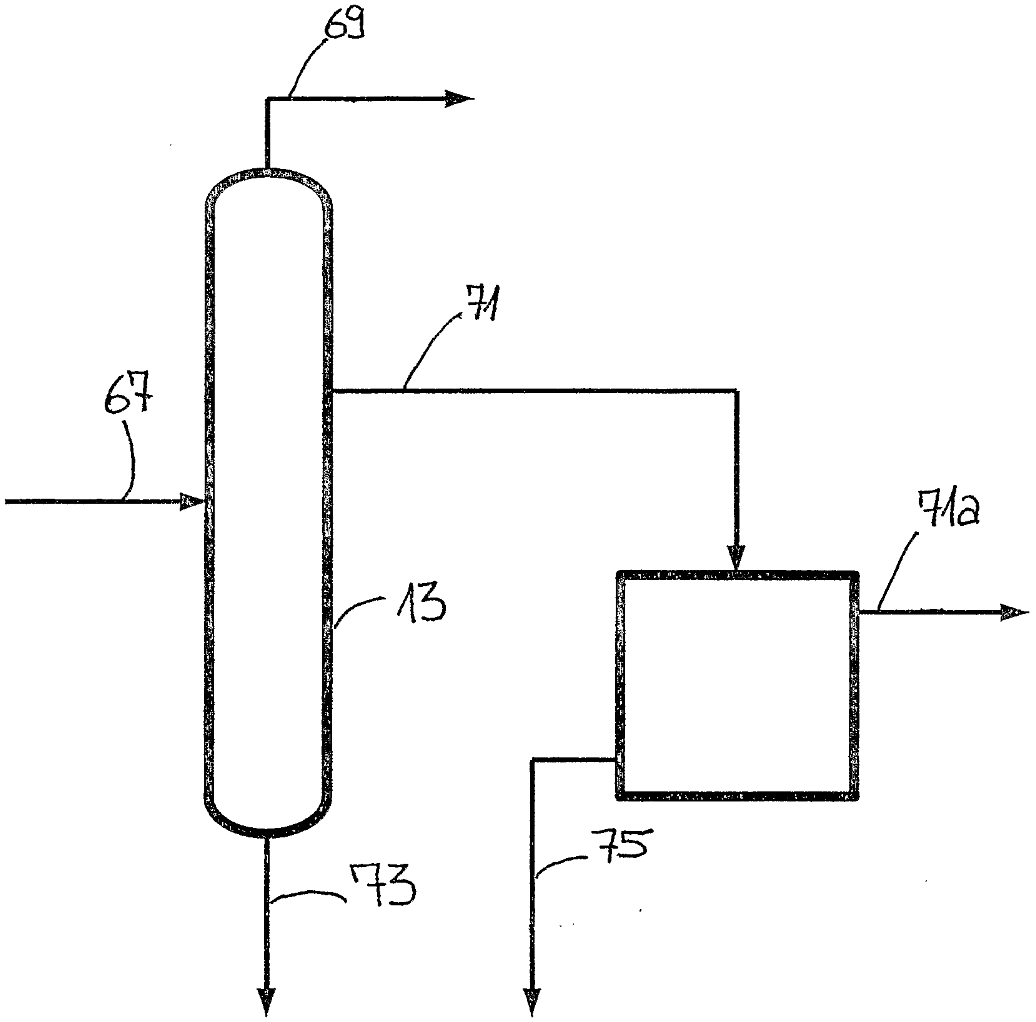

Fig. 3

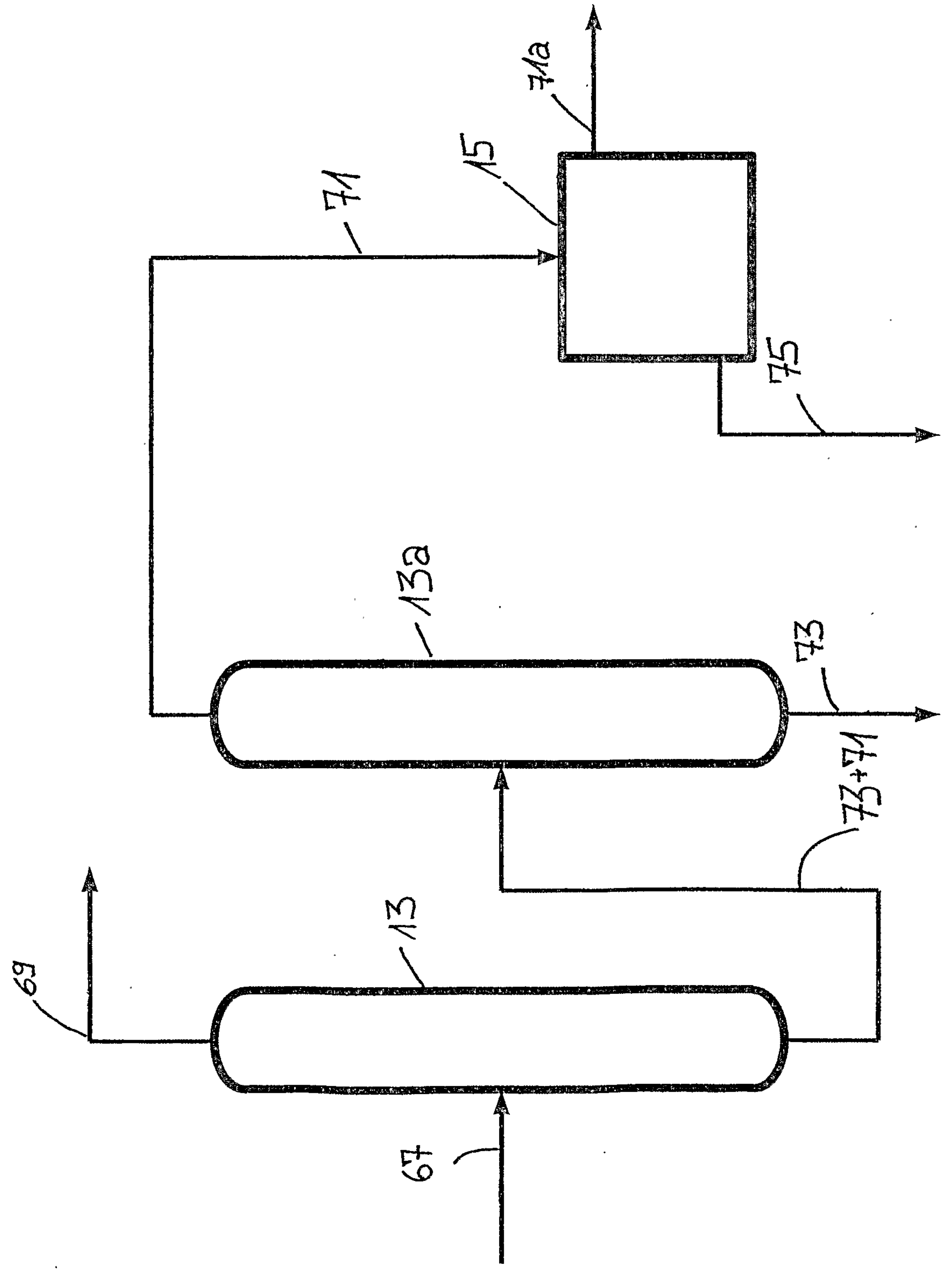

Fig. 4

INTERNATIONAL SEARCH REPORT

International Appl[illegible]on No
PCT/CH 03/00632

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C07C37/70 C07C37/84

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 094 722 A (SATO ET AL) 10 March 1992 (1992-03-10) claims ---	1-21
A	WO 00 14043 A (GENERAL ELECTRIC COMPANY) 16 March 2000 (2000-03-16) cited in the application claims -----	1-21

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
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- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search 14 January 2004	*Date of mailing of the international search report* 28/01/2004
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	Authorized officer O'Sullivan, P

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Appli[illegible]n No

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