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<p>(54) Title: PROCESS FOR PREPARING REFINED ACRYLIC ESTERS (57) Abstract The invention relates to a process for preparing refined acrylic esters comprising distilling an acrylic ester containing stream in the presence of a phenolic inhibitor and oxygen. The invention relates in particular to purified methyl methacrylate prepared from propyne.</p>		

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PROCESS FOR PREPARING REFINED ACRYLIC ESTERS

The invention relates to a process for preparing refined acrylic esters by distillation of an acrylic ester containing stream in the presence of a phenolic inhibitor. Acrylic esters can be represented by the general formula $\text{CH}_2=\text{CR}^1\text{COOR}^2$, wherein R^1 represents a hydrogen atom or an optionally substituted hydrocarbyl group, preferably a hydrogen atom or a methyl group and R^2 represents an optionally substituted hydrocarbyl group, typically an alkyl group such as a methyl group. The invention relates in particular to refined methyl acrylate and, more particularly, methyl methacrylate (hereinafter MMA).

Acrylic esters are valuable compounds that readily polymerize or copolymerize with a wide variety of other monomers. However, it is difficult to prepare acrylic esters of sufficient purity, e.g., freed from the corresponding acrylic acid, alcohol or water, without inadvertently converting part of the acrylic esters into oligomers, polymers or other undesirable products during their preparation.

The various methods for preparing acrylic esters are discussed in detail in volume 1 of the fourth edition of the Kirk-Othmer Encyclopedia of Chemical Technology (pp. 287-314, in particular Fig. 1 on p. 296). The same reference provides a typical process for preparing acrylic esters by esterification (pp. 301-302, Fig. 4) wherein acrylic acid, alcohol and a catalyst are fed to an esterification reactor. The esterification products, acrylic ester, excess alcohol and water of esterification, are taken overhead from the distillation column. The process uses additional wash and distillation columns

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to yield a refined acrylic ester. To minimize formation of the acrylic ester oligomers, polymers, etc., mild conditions and short residence times are maintained throughout the separation sections. In addition, conventional free-radical polymerization inhibitors are fed to each of the distillation columns. Finally, monomethyl ether of hydroquinone (10-100 ppmw, hereinafter MEHQ) is added to the end product as polymerization inhibitor and the esters are used in this form in most industrial polymerizations. The reference also discusses alternative routes to acrylic esters, based on acetylene, etc., that each incorporate a final (series of) distillation column(s) to separate refined acrylic ester. Indeed, as the alternative routes give rise to a multitude of difficult to separate side-products, distillation to separate refined acrylic ester is essential.

The Process Economics Program Report No. 11D, entitled METHACRYLIC ACID AND ESTERS" by SRI International of January 1993 provides a thorough review of the routes to MMA and methacrylic acid as well. Concerning MMA purification, suggested treatments include distillation, extraction, and treatment over ion-exchange resins or carbon beds. To avoid polymerization during purification, MMA must not be exposed to high temperatures, and distillation is generally done under vacuum and in the presence of polymerization inhibitors (pp. 5-4 to 5-5). In section 9 of the Report (MMA from propyne) it is proposed to distil under vacuum conditions to keep temperatures low and minimize decomposition or polymerization. In the Report it is suggested to add about 600 ppmw of MEHQ as polymerization inhibitor (p.9-5).

US-A-4,518,462 discloses a 2 column distillation process for removing water, methanol and methyl isobutyrate from MMA by using an n-hexane entrainer. In the examples 0.02% of hydroquinone and 0.03% of phenothiazine

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are used as polymerization inhibitors in the first distillation column, and 5% of hydroquinone is used in the second distillation column.

5 In Japan Kokai 2-17151 (1990, abstract) the distillation of impure MMA in the presence of 200 ppmw 4-benzoquinone plus 800 ppmw phenothiazine is described.

10 Neither of these documents teach or hint at measures to improve the efficiency of phenolic inhibitors, or identify the inhibitors used best in case the acrylic ester containing stream further comprises (the residue of) the catalyst system used to prepare the acrylic ester.

15 The inventors set out to determine the most optimal conditions for distillation of the acrylic ester, allowing for high throughputs by distilling at elevated temperatures, without significant loss of the acrylic ester. In particular, a process was looked for that allows distillation of the product stream of a carbonylation reaction further comprising (i) (residue of) the homogeneous catalyst system used to prepare the acrylic ester and
20 (ii) optionally an alcohol corresponding to the alcohol residue of the acrylic ester. More in particular, a process was looked for that allows the distillation of a product stream of a carbonylation reaction catalyzed by a catalyst system based on: (a) a Group VIII metal, preferably Pd; a ligand, preferably a phosphine mono- or bidentate ligand, and (c) a source of anions (Rippe Reactions, see chapter 3 of New Syntheses with Carbon Monoxide by J. Falbe, ISBN 3-540-09674-4). Such distillations are complicated by the presence of these catalyst components as
25 they may induce formation of the undesired oligomers, polymers etc.
30

35 The inventors surprisingly found that these objectives could be achieved by a process for preparing refined acrylic esters by distillation of an acrylic ester containing stream in the presence of a phenolic inhibi-

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tor, characterized in that the distillation is carried out in the presence of oxygen.

It has been found that the least formation of acrylic ester oligomers, polymers, etc. is obtained if the oxygen is present in an amount of 0.001 to 1.0 %v (on vapour phase). If less than the preferred amount is present, some oligomerization or polymerization still occurs, whereas using oxygen in a higher concentration is undesirable for safety and economic reasons.

Suitable phenolic inhibitors are known in the art and comprise for instance hydroquinone (hereinafter HQ) or 2,4,6-trimethylphenol; substituted hydroquinones such as 2,5-di-tert-butylhydroquinone, 2,5-dimethylhydroquinone, 2-methylhydroquinone, or alkyl ethers (preferably methyl ethers) of said (substituted) hydroquinone(s). Other examples are given in JP-A-05,320,095, wherein a process for preparing (meth)acrylic acid ester is described, carried out by reacting (meth)acrylic acid with alcohol in the presence of an acidic catalyst and a solvent, using as polymerization inhibitor an aromatic compound with at least one alkyl group and at least two hydroxyl groups per benzene ring. The suitability of preparing refined acrylic esters comprising distilling an acrylic ester containing stream in the presence of a phenolic inhibitor and oxygen, however, is not disclosed.

Benzoquinone or similar (carbonyl) compounds, although being well-known inhibitors, are not considered phenolic inhibitors within the definition of the present patent application. Indeed, US-A-3,794,567 illustrates the use of the polymerization inhibitors benzoquinone and hydroquinone monomethyl ether as such or in admixture in the presence of air (or oxygen) in the distillation of unsaturated acids (acrylic and methacrylic acid). However, the present inventors found benzoquinone to be an unsuitable inhibitor for the distillation of the acrylic

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esters, in particular in the presence of oxygen (cf. Table 1 supra), which is in contrast to the findings of this patent. Apparently, acrylic esters respond differently from acrylic acids to polymerization inhibitors during their distillation.

Preferably, the phenolic inhibitor is used at a concentration in the range of 200 to 5000 ppmw, more preferably in the range of 500 to 1500 ppmw (based on the acrylic ester). Using phenolic inhibitor outside the preferred range either increases the formation of the undesirable products, or merely increases the total costs.

The process is in particular suitable for preparing refined MMA. MMA and other acrylic esters may advantageously be prepared from acetocyanohydrin, ethene, propionic acid, propionaldehyde, methyl propionate or propyne using a homogeneous catalyst system. (cf. the SRI Report mentioned before).

Hydroquinone and substituted hydroquinones are the phenolic inhibitor of preference in case the catalyst system is based on: (a) a Group VIII metal, preferably Pd; (b) a ligand, preferably a mono- or bidentate phosphine ligand; and (c) a source of anions (for suitable catalyst systems and processes for preparing such acrylic esters see, for instance, European patent applications Nos. 0,186,228; 0,190,473; 0,194,707; 0,218,283; 0,218,284; 0,386,833; 0,386,834; 0,392,601; 0,441,446; 0,441,447; 0,489,472; 0,495,547; 0,499,329; 0,521,578; 0,565,199; and 0,571,044).

It is observed that optimal concentration of phenolic inhibitor depends on the amount of oxygen present, and vice versa. The higher, respectively lower the concentration of phenolic inhibitor, the lower, respectively higher is the required amount of oxygen.

The distillation may suitably be carried out at vacuum or (super)atmospheric pressures using a distillation

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column operating at a bottom temperature of 60-140 °C, preferably at a temperature in the range of 80-110 °C.

Preferably the phenolic inhibitor is introduced into the distillation column together with the acrylic ester containing stream. In addition or instead, it may be introduced at or near the top of the distillation column. The oxygen may be introduced advantageously at or near the bottom of the distillation column, either by a separate inlet or through leakage in case of vacuum distillation columns.

In case the acrylic ester containing stream further comprises (i) a homogeneous catalyst system and (ii) an alcohol corresponding to the alcohol residue of the acrylic ester, it is helpful to carry out the process in two steps. For instance, in step (1) an azeotrope of the alcohol (methanol) and acrylic ester is removed over the top of a first distillation column (to be recycled if the process is part of an integrated process further comprising a reactor where the acrylic ester is produced). The first bottom product is introduced in step 2 into a second distillation column, where heavy ends (oligomers and polymers) and (the residue of) the catalyst system is removed from the refined acrylate ester over the bottom of said distillation column and the refined ester is recovered over the top of said distillation column. Other configurations, changing the order for removal of the azeotrope and the heavy ends, will be apparent to the man skilled in the art.

It is within the gist of the invention to use a cascade of distillation columns (in series and/or parallel) instead of using a single distillation column. A particularly suitable process for removing the azeotrope is disclosed in European patent application No. 0,571,044 and (as part of a total process) in Figure 9.1 of the SRI report, page E-25.

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The invention further relates to a process for preparing refined acrylic esters by carbonylating an acetylenically unsaturated compound, preferably ethyne or propyne, with carbon monoxide and the corresponding alcohol, preferably methanol, in the presence of a catalyst system based on: (a) a Group VIII metal, preferably Pd; (b) a ligand, preferably a mono- or bidentate phosphine ligand; and (c) a source of anions, characterized in that the product stream of the carbonylation reaction is processed as set out above. Preferably, both processes are integrated such that the azeotrope stream recovered in step 1 in the two-step distillation set-up is reused. Optionally, also the catalyst system recovered from the bottom stream of the second distillation column of the two-step distillation set-up is reused.

The invention will be illustrated by the following model examples.

Example 1

MMA, to which 500 ppmw inhibitor was added, was kept at 80 °C under a flow of nitrogen gas or air (modelling the distillation conditions). The MMA was analyzed on the presence of ppmw PMMA (visual detection limit of 500 ppmw PMMA by observation of haziness using 2 %wt MMA in methanol, determining the number of days required before PMMA could be detected). The results are set out in Table 1. From these results it may be concluded that in the presence of oxygen, the phenolic inhibitors showed improved performance, whereas the performance of p-benzoquinone decreased in the presence of oxygen. Most marked improvements were found for 2,4,6-trimethylphenol, HQ and MEHQ, although "IONOL-K" and "IONOL-CP" (trademarks for 4-methyl-2,6-di-tert-butylphenol and 2,4-dimethyl-6-tert-butylphenol respectively) also performed well in the presence of oxygen.

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Example 2

A synthetic feed (modelling the crude product obtained in an MMA from propyne production process) comprising MMA, 100 or 1000 ppmw inhibitor, and a catalyst system comprising, if present, 40 ppmw Pd, Pd/PN/MeSA in molar ratio 1:10:5 or 1:10:20 (PN stands for 2-pyridyl-diphenylphospine; MeSA stands for methanesulphonic acid) was kept at 80 °C under a flow of 0.1 %v O₂/N₂ (modelling the distillation conditions). The feed was analyzed on ppmw PMMA (detection limit of 10 ppmw PMMA by GPC analysis). The results are set out in Table 2. From these results it may be concluded that in absence of the catalyst system, "IONOL-CP" and "IONOL-K" perform similar to HQ and substantially better than MEHQ. However, in the presence of the catalyst system HQ performs substantially better than the other phenolic inhibitors.

Table 1

Inhibitor	Stability at 80 °C under nitrogen in days	Stability at 80 °C under air in days
HQ	1	29
4-tert-butylcatechol	6	14
2,4-di-tert-butylphenol	1	16
4-methyl-2,6-di-tert-butylphenol	2-4	19
2,4-dimethyl-6-tert-butylphenol	13	43
2,4,6-trimethylphenol	1	> 55
MEHQ	1	26
p-benzoquinone	8	2-4

Table 2

Pd conc. (ppmw)	Pd/PN/MeSA (molar ratio)	inhibitor conc. (ppmw)	inhibitor type		
			HQ	MEHQ	"IONOL-CP" *
			(days with < 10 ppmw or ppmw PMMA after 1 day)		
0	no additives	100	> 7 days	2 days	> 6 days
40	1:10:5	100	4,800	29,000	17,000
40	1:10:20	1000	640	solid only	16000
					> 11 days 12,000 19000

* trademarks

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Example 3

A synthetic feed comprising MMA, 100 ppmw HQ, and a catalyst system comprising, if present, 40 ppmw Pd, Pd/PN/MeSA in molar ratio 1:10:5 was kept at 80 °C under a flow of 0.1 %v O₂/N₂. The feed was again analyzed on ppmw PMMA. The results are set out in Table 3. From these results it may be concluded that the problem of PMMA formation is particular great in the presence of the complete catalyst system.

Example 4

A synthetic feed comprising MMA, a variable amount of HQ, and a catalyst system comprising 40 ppmw Pd, Pd/PN/MeSA in molar ratio of 1:30:35 was kept at 80 °C under a flow of 0.1 %v or 20 %v O₂. The feed was analyzed on ppmw PMMA (detection limit of 10 ppmw PMMA by GPC analysis). The results are set out in Table 3. From these results it may be concluded that the presence of both O₂ and HQ are required, and that to achieve the same result in PMMA reduction either a (relatively) large amount of O₂ or a (relatively) large amount of HQ may be used.

Example 5

A synthetic feed was used comprising 83.8 %wt MMA, 15.1 %wt MeOH, 1.0 %wt methyl crotonate, a catalyst system comprising 10 ppmw Pd (fed as palladium(II) acetate), Pd/PN/MeSA in molar ratio 1:30:35 and 500 or 1000 ppmw HQ.

The feed was subjected to a two-step distillation set-up comprising two distillation columns in series, operating at the following conditions: 80-100 °C bottoms temperature; air flow in both bottoms approximately 0.3 NL (NL is litre at 1 bar, 20 °C) per hour (0.05-0.1 %v O₂ in vapour phase); a feed flow of 105 millilitres per hour (comprising azeotrope 25; MMA 70; heavy ends 10); and residence times in the bottoms of 3-4 hours in the first distillation column and 25-50 hours in the second distil-

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lation column.

From the results (Table 5) it may be concluded that PMMA formation may be reduced in a continuous distillation to an acceptable level. Higher PMMA levels are found in the second bottoms, due to concentration. There is only a small effect of the temperature on PMMA production.

Example 6

Example 5 was repeated, however, with the difference that instead of a synthetic feed, crude product originating from an MMA from propyne production process was used. This feed, to which 500 ppmw HQ was added, comprised 72.7 %wt MMA, 25.5 %wt MeOH, 0.8 %wt methyl crotonate, and catalyst system (10 ppmw Pd, Pd/PN/MeSA mol ratio 1:30:30).

The feed flow amounted to 140 millilitres per hour (comprising azeotrope 55; MMA 75; heavy ends 10). The results (Table 6) illustrate the suitability of the present process.

Table 3

presence of:			reaction time	PMMA conc.
Pd	PN ligand	MeSA	(days)	(ppmw)
-	-	-	7	< 10
+	-	-	7	< 10
-	+	-	7	< 10
-	-	+	7	< 10
+	+	-	3	50
-	+	+	10	< 10
+	-	+	10	< 10
+	+	+	1	4800

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Table 4

HQ (ppmw)	PMMA conc. (ppmw)	
	0.1 %v O ₂	20 %v O ₂
50	7,100	1,600
100	7,100	40
250	890	< 10
750	80	< 10
1000	100	< 10
1500	< 10	< 10

Table 5

HQ conc. (ppmw/feed)	PMMA conc. in 1st/2nd column bottoms (ppmw/ppmw)					
	80 °C		90 °C		100 °C	
500	30	3,100	< 10	1,100	30	12,500
1000	20	520	< 10	710	40	740

Table 6

bottoms tempera- ture	air flow	PMMA conc. in 1st/2nd column bottoms (ppmw/ppmw)		
		feed	1st bottom	2nd bottom
(°C)	(NL per hour)			
80	0.5	820	1,460	17,600
100	3.0	820	1,060	8,900
100	1.5	820	1,200	11,000
mass balance*		820	1,250	10,500

* calculated amount of PMMA present in the bottoms if no PMMA is formed, but merely concentrated.



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C L A I M S

1. A process for preparing refined acrylic esters by distillation of an acrylic ester containing stream in the presence of a phenolic inhibitor, characterized in that the distillation is carried out in the presence of oxygen.
2. A process as claimed in claim 1, wherein the oxygen is present in an amount of 0.001 to 1.0 %v (on vapour phase).
3. A process as claimed in claim 1 or 2, wherein the phenolic inhibitor is used at a concentration in the range of 200 to 5000 ppmw, preferably in the range of 500 to 1500 ppmw (based on the acrylic ester).
4. A process as claimed in any one of claims 1 to 3, wherein the phenolic inhibitor is hydroquinone or an optionally substituted hydroquinone.
5. A process as claimed in any one of claims 1 to 4, wherein the acrylic ester containing stream further comprises (i) a homogeneous catalyst system for making methyl methacrylate from acetocyanohydrin, ethene, propionic acid, propionaldehyde, methyl propionate or propyne and (ii) optionally an alcohol corresponding to the alcohol residue of the acrylic ester.
6. A process as claimed in claim 5, wherein the catalyst system is based on: (a) a Group VIII metal, preferably Pd; (b) a ligand, preferably a mono- or bidentate phosphine ligand; and (c) a source of anions.
7. A process as claimed in any one of claims 1 to 6, wherein the distillation is carried out in a distillation column operating at a temperature in the range of 60 to 140 °C, preferably at a temperature in the range of 80 to 110 °C.

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8. A process as claimed in claim 7, wherein the phenolic inhibitor is introduced into the distillation columns together with the acrylic ester containing stream.

9. A process as claimed in claim 7 or 8, wherein the phenolic inhibitor is introduced at or near the top of the distillation column.

10. A process as claimed in any one of claims 7 to 9, wherein the oxygen is introduced at or near the bottom of the distillation column.

11. A process as claimed in any one of claims 1 to 10, wherein the acrylic ester containing stream further comprises (i) a homogeneous catalyst system for making methyl methacrylate from acetocyanohydrin, ethene, propionic acid, propionaldehyde, methyl propionate or propyne and (ii) optionally an alcohol corresponding to the alcohol residue of the acrylic ester, and the distillation is carried out in two steps whereby in step (1) an azeotrope of the alcohol and acrylic ester is removed over the top of a first distillation column, the first bottom product is introduced into a second distillation column where heavy ends and the (residue of the) catalyst system is removed from the refined acrylic esters over the bottom of said distillation column and the refined acrylate ester is recovered over the top of said distillation column.

12. A process as claimed in any one of claims 1 to 11, wherein the distillation or each step of a two step distillation set-up is carried out in a cascade of distillation columns.

13. A process as claimed in any one of claims 1 to 12, wherein the acrylic ester is methyl methacrylate or methyl acrylate, preferably methyl methacrylate.

14. A process for preparing refined acrylic esters by carbonylating an acetylenically unsaturated compound, preferably ethyne or propyne, with carbon monoxide and an

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5 alcohol, preferably methanol, in the presence of a catalyst system based on: (a) a Group VIII metal, preferably Pd; (b) a ligand, preferably a mono- or bidentate phosphine ligand; and (c) a source of anions, characterized in that the product stream of the carbonylation reaction is processed as claimed in any one of claims 1 to 13.

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REVISED CLAIMS

1. A process for preparing refined acrylic esters by distillation of an acrylic ester containing stream in the presence of a phenolic inhibitor and oxygen, characterized in that:

- 5 (1) the acrylic ester containing stream further comprises (i) a homogeneous catalyst system, wherein the catalyst system is based on: (a) a Group VIII metal, preferably Pd; (b) a ligand, preferably a mono- or bidentate phosphine ligand; and (c) a source of anions
10 and (ii) optionally an alcohol corresponding to the alcohol residue of the acrylic ester; and
(2) wherein the phenolic inhibitor is hydroquinone.
2. A process as claimed in claim 1, wherein the oxygen is present in an amount of 0.001 to 1.0 %v (on vapour
15 phase).
3. A process as claimed in claim 1 or 2, wherein the phenolic inhibitor is used at a concentration in the range of 200 to 5000 ppmw, preferably in the range of 500 to 1500 ppmw (based on the acrylic ester).
- 20 4. A process as claimed in any one of claims 1 to 3, wherein the distillation is carried out in a distillation column operating at a temperature in the range of 60 to 140 °C, preferably at a temperature in the range of 80 to 110 °C.
- 25 5. A process as claimed in claim 4, wherein the phenolic inhibitor is introduced into the distillation columns together with the acrylic ester containing stream.
6. A process as claimed in claim 4 or 5, wherein the phenolic inhibitor is introduced at or near the top of
30 the distillation column.



7. A process as claimed in any one of claims 4 to 6, wherein the oxygen is introduced at or near the bottom of the distillation column.

5 8. A process as claimed in any one of claims 1 to 7, wherein the acrylic ester containing stream further comprises (i) a homogeneous catalyst system for making methyl methacrylate from acetocyanohydrin, ethene, propionic acid, propionaldehyde, methyl propionate or propyne and (ii) optionally an alcohol corresponding to
10 the alcohol residue of the acrylic ester, and the distillation is carried out in two steps whereby in step (1) an azeotrope of the alcohol and acrylic ester is removed over the top of a first distillation column, the first bottom product is introduced into a second distillation
15 column where heavy ends and the (residue of the) catalyst system is removed from the refined acrylic esters over the bottom of said distillation column and the refined acrylate ester is recovered over the top of said distillation column.

20 9. A process as claimed in any one of claims 1 to 8, wherein the distillation or each step of a two step distillation set-up is carried out in a cascade of distillation columns.

25 10. A process as claimed in any one of claims 1 to 9, wherein the acrylic ester is methyl methacrylate or methyl acrylate, preferably methyl methacrylate.