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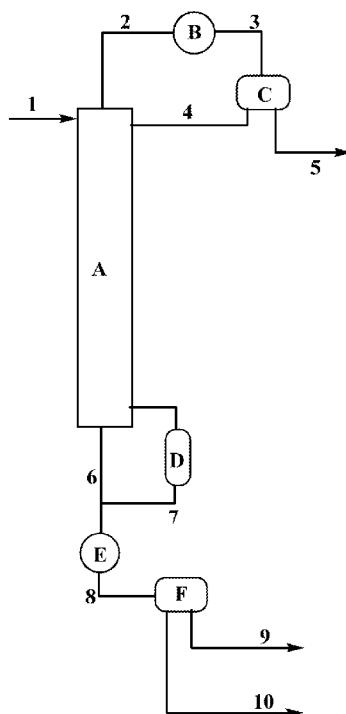
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*[Continued on next page]*

(54) Title: PROCESS FOR PURIFICATION OF METHYL METHACRYLATE

**FIGURE 1**

(57) **Abstract:** A process for purifying methyl methacrylate by feeding a product mixture comprising methanol, methyl methacrylate and alkali metal salts thereof, methacrolein, water and heavy byproducts to a distillation column having at least 15 trays. The product mixture and a C<sub>6</sub>-C<sub>7</sub> hydrocarbon enter the distillation column above the middle of the distillation column. An overhead stream comprising C<sub>6</sub>-C<sub>7</sub> hydrocarbon, methacrolein, methanol, water and methyl methacrylate and a bottoms stream comprising water, methyl methacrylate and its alkali metal salt and heavy byproducts are removed from the column.



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## PROCESS FOR PURIFICATION OF METHYL METHACRYLATE

### BACKGROUND OF THE INVENTION

The invention relates to a process for purification of a methyl methacrylate (MMA) 5 reaction product from the effluent of an oxidative esterification reactor (OER).

The use of oxidative esterification to prepare MMA from methacrolein and methanol is well known. For example, US4518462 discloses a process having a methanol recovery column using hexane as an entrainer. However, this process is not suitable for reaction products which contain MMA salts. There is a need for a more efficient process for 10 separating the components of reaction products resulting from preparation of methyl methacrylate.

### SUMMARY OF THE INVENTION

The present invention is directed to a process for purifying methyl methacrylate; 15 said method comprising: (a) feeding a reaction product mixture comprising methanol, methyl methacrylate and alkali metal salts thereof, methacrolein, water and heavy byproducts to a distillation column having at least 15 trays; wherein said reaction product mixture and a C<sub>6</sub>-C<sub>7</sub> hydrocarbon enter the distillation column above the middle of the distillation column; (b) removing an overhead stream comprising C<sub>6</sub>-C<sub>7</sub> hydrocarbon, 20 methacrolein, methanol, water and methyl methacrylate; and (c) removing a bottoms stream comprising water, methyl methacrylate and its alkali metal salt and heavy byproducts.

### BRIEF DESCRIPTION OF THE DRAWING

The Figure is a schematic of a process of the invention.

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### DETAILED DESCRIPTION OF THE INVENTION

All percentage compositions are weight percentages (wt%), and all temperatures are in °C, unless otherwise indicated. Heavy byproducts are byproducts of the OER which have higher boiling points than methyl methacrylate, and which comprise oligomers of methyl 30 methacrylate in addition to unknown products. Oligomers of methyl methacrylate comprise the dimer of methyl methacrylate and smaller amounts of higher oligomers, including, e.g., the trimer. Preferably, alkali metal salts are sodium or potassium salts, preferably sodium.

The C<sub>6</sub>-C<sub>7</sub> hydrocarbon functions as an entrainer. It is believed that it breaks the methanol/MMA azeotrope, allowing removal and recovery of methanol. Preferably, the C<sub>6</sub>-

C<sub>7</sub> hydrocarbon is aliphatic. Preferably, the C<sub>6</sub>-C<sub>7</sub> hydrocarbon is a saturated hydrocarbon, preferably an acyclic alkane. In one preferred embodiment, a mixture of C<sub>6</sub>-C<sub>7</sub> hydrocarbons is used. Preferably, the C<sub>6</sub>-C<sub>7</sub> hydrocarbon or mixture thereof has an atmospheric pressure (101 kPa) boiling point from 65 to 100°C, preferably at least 67°C; preferably no greater than 90°C, preferably no greater than 80°C, preferably no greater than 75°C. Preferably, the C<sub>6</sub>-C<sub>7</sub> hydrocarbon is n-hexane.

5 Preferably, the distillation column has at least 20 trays, preferably at least 25; preferably no more than 40 trays, preferably no more than 35 trays. Preferably, the point at which the reaction product mixture enters the distillation column is in the highest 40% of 10 the trays, preferably the highest 30%, preferably the highest 20%, preferably the highest 10%, preferably the highest 7%. Preferably, the point at which the reaction product mixture enters the distillation column is in the highest ten trays, preferably in the highest eight trays, preferably in the highest six trays, preferably in the highest four trays, preferably in the highest three trays, preferably in the highest two trays, preferably in the top tray.

15 Preferably, the reaction product mixture comprises at least 0.8 wt% methyl methacrylate alkali metal salts, preferably at least 1 wt%, preferably at least 1.5 wt%, preferably at least 1.8 wt%; preferably no more than 3 wt%, preferably no more than 2.5 wt%, preferably no more than 2 wt%. Preferably, the reaction product mixture comprises from 40 to 80 wt% methanol, preferably from 45 to 70 wt%, preferably from 50 to 68 wt%. Preferably, the 20 reaction product mixture comprises from 5 to 40 wt% methyl methacrylate, preferably from 10 to 35 wt%, preferably from 15 to 32 wt%. Preferably, the reaction product mixture comprises from 1 to 10 wt% water, preferably from 3 to 9 wt%, preferably from 4 to 8 wt%. Preferably, the amount of the C<sub>6</sub>-C<sub>7</sub> hydrocarbon(s) which enters the column as reflux is from 2 to 10 times the amount of methanol in the product mixture, preferably 3 to 5 times.

25 Preferably, when additional C<sub>6</sub>-C<sub>7</sub> hydrocarbon needs to be added, it enters the distillation column in the highest ten trays, preferably in the highest eight trays, preferably in the highest six trays, preferably in the highest four trays, preferably in the highest three trays, preferably in the highest two trays, preferably in the top tray.

In a preferred embodiment, prior to the process described herein, the direct product 30 from the OER passes through a separate distillation column to remove light components, i.e., those having higher vapor pressure than methanol. The light components principally comprise methyl formate. Typical levels of methyl formate in the direct product are from 1 to 6 wt% and the reaction product mixture fed to the distillation column in the method of this invention typically contains no more than 1 wt% methyl formate.

The overhead stream passes through a condenser and then enters a water separator, from which the organic phase is returned to the same section of the distillation column where the product mixture enters, and the aqueous phase is removed. Preferably, water is added to the water separator. Preferably, the amount of water added to the water separator 5 is 0.2 to 1 times the amount of the overhead stream, preferably 0.25 to 0.6 times. Preferably, the bottoms stream enters a water separator after passing through a heat exchanger to cool it. The organic phase is predominantly MMA and preferably is processed further to obtain high-purity MMA. The aqueous phase contains methyl methacrylate alkali metal salt and water.

10 Water may be decanted from the stream by the means of standard methods. In one preferred embodiment, by means of a vessel that contains a vertical baffle or a series of baffles and is sized sufficiently that the organic and aqueous phase separate into individual phases. The lighter phase organic proceeds over the vertical baffle and the heavier water phase flows underneath the baffle. The separated liquids are withdrawn from the sections of 15 the vessel that have accumulated the overflow and underflow of each phase.

16 The temperature and pressure in the distillation column is dependent on the composition of the material being distilled. In a preferred embodiment of the invention, the column is operated at reduced pressure, such as from about 100 to about 760 mmHg (13 to 101 kPa), or from 200 to 400 mmHg (26 to 53 kPa). Preferably, the column pressure is 20 adjusted to keep the bottoms temperature below 120°C, preferably below 100°C.

Preferably, polymerization inhibitor is added to the column to minimize polymerization of MMA. Preferably, inhibitor is added above the middle of the column, preferably in the reflux. Amounts of inhibitor typically are small and types and typical use amounts are well known in the field.

25 The type of distillation column can be selected according to criteria well known to those skilled in the art.

26 The Figure depicts a distillation column **A** into which the product mixture **1** is introduced into the column. Bottoms, **6** from the column are split, with stream **8** passing through a heat exchanger **E**, with organic stream **9** and aqueous stream **10** removed from the 30 column and recycle **7** returned to the column through reboiler **D**. Overhead stream **2** leaves the column at the top and passes through condenser **B** and the resulting stream **3** enters splitter **C**, with aqueous phase **5** removed from the column and organic phase **4** returned to the column.

## EXAMPLES

Example 1

This experiment is carried out using the process configuration shown in Figure 1. The distillation column is a 28 mm i.d. 30-tray Oldershaw column, and n-hexane is employed as the entrainer solvent. A steam-heated thermosiphon reboiler is used to provide the boil-up in the column. The pressure at the top of the column is 700 mmHg absolute. The overhead temperature is 48°C, and the bottoms temperature is 83°C.

A mixture containing 29.9% MMA, 58.1% methanol, 2.1% methacrolein, 7.1% water, and 1.2% sodium methacrylate, with the balance being lights (higher vapor pressure than methanol) and organic heavies (lower vapor pressure than MMA) is fed through line 1 at a rate of 197 g/hr to the top tray of the distillation column.

Surprisingly, no salt precipitation is observed on the trays or in the reboiler after 8 hours of run time. No sodium methacrylate is detected in the bottoms organic crude MMA stream so, further downstream processes will have no difficulty with salt precipitation.

15 Table 1 – Stream Compositions and Process Conditions for Ex. 1

Component	Line #						
	1	3	6	7	8	11	12
Water	7.10%		99.96%	0.0%	61.1%	1.2%	84.40%
Methanol	58.10%	99%		0.2%	36.7%		
Methacrolein	2.10%			1.6%	0.7%		
Methyl Methacrylate	29.90%			8.4%	1.1%	97.0%	1.40%
Sodium Methacrylate	1.20%					trace	14.10%
Hexane				89.50%			
Phenothiazine		1%			NA	NA	NA
4-Hydroxy Tempo	0.04%		0.04%		NA	NA	NA
Flow (g/hr)	197.0	5.0	187.8	371.5	315.0	58.1	16.8

NA - not applicable

Example 2

An ASPEN simulation of feed location in a 30-tray distillation column (tray 1 is the top tray), assuming 60% tray efficiency produced the following results for the %MMA recycled to the column.

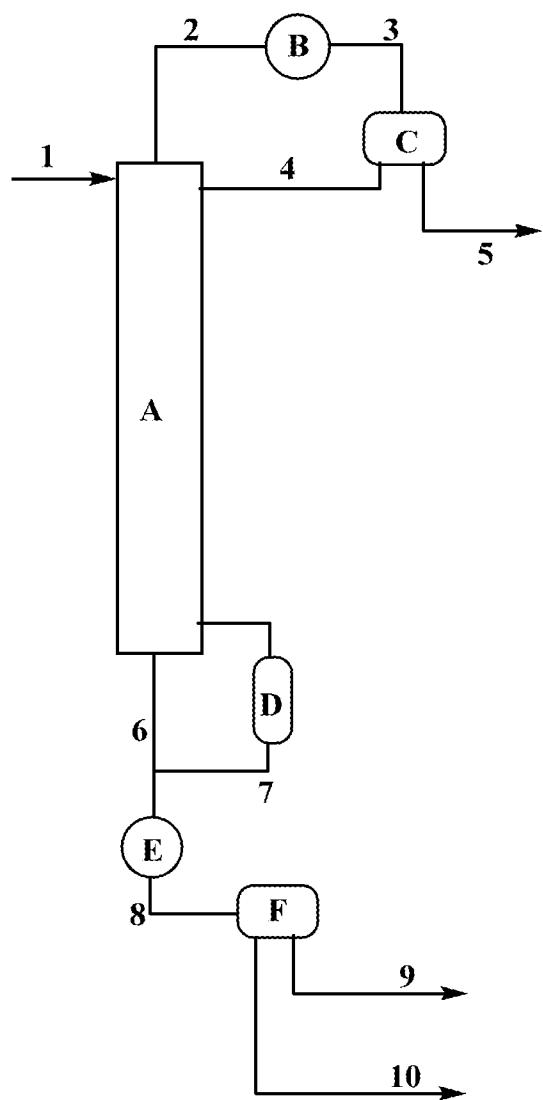
5

Feed Tray	% MMA Recycled
1	5.6%
6	7.3%
11	7.4%
16	8.0%
21	9.8%

The efficiency of the column increases as the location of the reaction product mixture feed rises in the column.

## CLAIMS:

1. A process for purifying methyl methacrylate; said method comprising: (a) feeding a reaction product mixture comprising methanol, methyl methacrylate and alkali metal salts thereof, methacrolein, water and heavy byproducts to a distillation column having at least 15 trays; wherein said reaction product mixture and a C<sub>6</sub>-C<sub>7</sub> hydrocarbon enter the distillation column above the middle of the distillation column; (b) removing an overhead stream comprising C<sub>6</sub>-C<sub>7</sub> hydrocarbon, methacrolein, methanol, water and methyl methacrylate; and (c) removing a bottoms stream comprising water, methyl methacrylate and its alkali metal salt and heavy byproducts.
2. The process of claim 1 wherein the reaction product mixture comprises at least 0.8 wt% of the sodium salt of methyl methacrylate.
3. The process of claim 2 wherein the reaction product mixture comprises from 1 to 10 wt% water.
4. The process of claim 3 wherein the reaction product mixture enters the distillation column in the highest 30% of the trays.
5. The process of claim 4 wherein C<sub>6</sub>-C<sub>7</sub> hydrocarbon is a saturated hydrocarbon having an atmospheric pressure boiling point from 65 to 100°C.
6. The process of claim 5 wherein a portion of the overhead stream returns to the distillation column in the highest 30% of the trays and the amount of the C<sub>6</sub>-C<sub>7</sub> hydrocarbon in said overhead stream which enters the column is from 2 to 10 times the amount of methanol in the reaction product mixture.
7. The process of claim 6 wherein the reaction product mixture enters the distillation column in the highest 20% of the trays.
8. The process of claim 7 wherein the distillation column has from 20 to 40 trays.
9. The process of claim 8 wherein the reaction product mixture enters the distillation column in the highest four trays.

**FIGURE 1**

# INTERNATIONAL SEARCH REPORT

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PCT/US2016/065324

**A. CLASSIFICATION OF SUBJECT MATTER**  
INV. C07C67/39 C07C67/54 C07C69/54  
ADD.

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)  
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 practicable, search terms used)

EPO-Internal, WPI Data, CHEM ABS Data

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	CN 103 833 551 A (ENGINEERING DESIGN RES INST CO LTD OF EAST CHINA UNIVERSITY) 4 June 2014 (2014-06-04) [0074], [0091]; claim 1; figure 1 -----	1-9
A	EP 0 390 577 A2 (MITSUI TOATSU CHEMICALS [JP]; KURARAY CO [JP]) 3 October 1990 (1990-10-03) claim 1; figure 1 -----	1-9
A	US 4 518 462 A (AOSHIMA ATSUSHI [JP] ET AL) 21 May 1985 (1985-05-21) cited in the application claim 1 -----	1-9
A	US 3 431 181 A (BOUNIOT ALBERT) 4 March 1969 (1969-03-04) the whole document -----	1-9



Further documents are listed in the continuation of Box C.



See patent family annex.

\* Special categories of cited documents :

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# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No PCT/US2016/065324
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Patent document cited in search report	Publication date	Patent family member(s)			Publication date
CN 103833551	A	04-06-2014	NONE		
EP 0390577	A2	03-10-1990	CA 2012935 A1 CN 1046518 A DE 69010046 D1 DE 69010046 T2 EP 0390577 A2 US 5028735 A	30-09-1990 31-10-1990 28-07-1994 13-10-1994 03-10-1990 02-07-1991	
US 4518462	A	21-05-1985	DE 3161884 D1 EP 0044409 A1 US 4518462 A	16-02-1984 27-01-1982 21-05-1985	
US 3431181	A	04-03-1969	BE 700290 A CH 474462 A DE 1643121 A1 ES 342170 A1 FR 93305 E FR 1490688 A GB 1166928 A NL 6707669 A SE 350024 B US 3431181 A	21-12-1967 30-06-1969 09-03-1972 01-10-1968 14-03-1969 04-08-1967 15-10-1969 27-12-1967 16-10-1972 04-03-1969	