



159159

DESCRIPTION

METHOD FOR SUPPRESSING PRODUCTION OF HEAVY COMPONENT OF
METHYL ETHYL KETONE

5

TECHNICAL FIELD

[0001]

The invention relates to a method for suppressing
production of a heavy component of methyl ethyl ketone.

10 More particularly, the invention relates to a method for
suppressing production of a heavy component by dimerization
of methyl ethyl ketone, and also relates to equipment for
purification or storage of methyl ethyl ketone.

15

BACKGROUND ART

[0002]

Methyl ethyl ketone (MEK) is a useful compound mainly
as a solvent, and can be synthesized by a dehydrogenation
reaction of 2-butanol (see non-Patent Document 1, for
20 example). The production process of methyl ethyl ketone
will be described briefly below.

[0003]

FIG. 1 is a schematic flow chart showing a production
process of methyl ethyl ketone.

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2-butanol as a raw material (indicated as "SBA" in
the figure) undergoes a dehydrogenation reaction in a
dehydrogenation reactor 10 to be methyl ethyl ketone



(indicated as "MEK" in the figure). Then, the methyl ethyl ketone is sent to an MEK fractionating tower 20 where the methyl ethyl ketone and the raw material are separated. The methyl ethyl ketone is taken out at the top of the tower, while the 2-butanol is taken out at the bottom of the tower. The recovered 2-butanol is reused as a raw material. The fractionated methyl ethyl ketone is then dehydrated in a dehydration tower 30 since it contains a small amount of water as a by-product. Subsequently, the methyl ethyl ketone is sent to a purification tower 40 where a heavy component formed by the dimerization of the methyl ethyl ketone or the like is removed, whereby methyl ethyl ketone having a degree of purity enough to be used as a product is produced, and then stored in storage equipment 50.

[0004]

Methyl ethyl ketone synthesized and purified in the above-mentioned process has the following problems.

1. Methyl ethyl ketone may not meet the product specification since the amount of the heavy component increases during storage.
2. Contrary to the belief that methyl ethyl ketone purified by separation in a purification tower contains almost no heavy component, a small amount of a heavy component still remains even after purification.

Non-patent Document 1: Journal of Chemical Engineering of Japan, Vol. 50, issue 8 (1986), p.565

[0005]

The invention has been made in view of the above-mentioned problems. An object of the invention is to provide a method for suppressing production of a heavy
5 component which deteriorates purity of methyl ethyl ketone.

DISCLOSURE OF THE INVENTION

[0006]

The inventors made extensive studies to solve the
10 above-mentioned problems, and paid attention to materials of equipment used in a purification process or in a storage part. In a purification or storage equipment, a low-cost material such as carbon steel is generally used insofar as a corrosive component such as an acid is not treated. In
15 the production of methyl ethyl ketone, carbon steel has been used since it does not contain components which cause corrosion of equipment.

However, it has been confirmed that, when carbon steel is oxidized, methyl ethyl ketone is dimerized since
20 an iron oxide serves as a catalyst. The inventors have found that dimerization of methyl ethyl ketone can be prevented by use of an appropriate material for equipment which is to be in contact with methyl ethyl ketone. The invention has been made based on this novel finding.

25 [0007]

The invention provides the following method for suppressing production of a heavy component of methyl ethyl

ketone.

1. A method for suppressing production of a heavy component of methyl ethyl ketone comprising using a dimerizing inhibitor material at least in a surface of purification or storage equipment which is to be in contact with methyl ethyl ketone.

2. The method for suppressing production of a heavy component of methyl ethyl ketone according to 1, wherein the dimerizing inhibitor material is zinc, aluminum, a zinc-aluminum alloy, tin, stainless steel, a fluorine-based resin or a polyolefin resin.

3. The method for suppressing production of a heavy component of methyl ethyl ketone according to 2, wherein the dimerizing inhibitor material used in the purification equipment is stainless steel.

4. The method for suppressing production of a heavy component of methyl ethyl ketone according to 3, wherein the purification equipment is a condenser which cools methyl ethyl ketone and/or a receiver which temporarily receives methyl ethyl ketone.

5. The method for suppressing production of a heavy component of methyl ethyl ketone according to 2, wherein the dimerizing inhibitor material used in the storage equipment is zinc, aluminum, a zinc-aluminum alloy, or tin.

6. A purification or storage equipment for methyl ethyl ketone comprising at least a surface to be in contact with methyl ethyl ketone made of a dimerizing inhibitor

material.

[0008]

In the method for suppressing production of a heavy component of methyl ethyl ketone of the invention, dimerization of methyl ethyl ketone in a purification process or during storage can be prevented. Therefore, the method of the invention is suitable to maintain the quality of products.

10 BRIEF DESCRIPTION OF THE DRAWINGS

[0009]

FIG. 1 is a schematic flow chart showing the purification process of methyl ethyl ketone.

FIG. 2 is a schematic flow chart showing the production process of methyl ethyl ketone.

BEST MODE FOR CARRYING OUT THE INVENTION

[0010]

The method for suppressing production of a heavy component of methyl ethyl ketone of the invention comprises using a dimerizing inhibitor material at least in a surface of a purification or storage equipment which is to be in contact with methyl ethyl ketone.

FIG. 1 is a schematic flow chart showing a purification process of methyl ethyl ketone. FIG. 1 shows a purification process of methyl ethyl ketone which has been dehydrated in a dehydration tower 30 shown in FIG. 2.

Dehydrated methyl ethyl ketone is distilled in a purification tower 40, and recovered in the form of a gas from the top of the tower. The methyl ethyl ketone in the form of a gas is cooled by a condenser 42 to be liquefied.

5 The resultant liquid is received in a receiver 44. The methyl ethyl ketone accumulated in the receiver 44 is sent to a purification tower 40 again if necessary, where a heavy component is removed till the methyl ethyl ketone satisfies the product specification. If the methyl ethyl
10 ketone meets the product specification, the methyl ethyl ketone is then cooled to normal temperatures by a cooler 46 and stored in storage equipment 50. The methyl ethyl ketone is transported using a pump P.

[0011]

15 In the method for suppressing production of a heavy component of methyl ethyl ketone of the invention, a dimerizing inhibitor material is used in purification equipment such as the condenser 42, the receiver 44 and the cooler 46, and/or storage equipment such as a storage tank.

20 As examples of the inhibitor materials, metal materials such as zinc, tin, stainless steel, aluminum, and a zinc-aluminum alloy; resin materials such as a fluorine-based resin such as polytetrafluoroethylene, and polyolefin resins; and the like can be given. Also, a silica coating
25 film or a coating film of a hydroxide of zinc or aluminum obtained by treating zinc or aluminum with water may be used (sealing).

A dimerizing inhibitor material may be used at least in a surface where equipment is to be in contact with methyl ethyl ketone. Specifically, entire equipment may be formed of a dimerizing inhibitor material, or alternatively,
5 a surface to be in contact with methyl ethyl ketone may be plated or thermally sprayed, whereby a film of a dimerizing inhibitor material is formed thereon.

[0012]

In the invention, the dimerizing inhibitor material
10 used in the purification equipment may preferably be stainless steel. In the purification process, methyl ethyl ketone is kept at a high temperature (80°C or higher) till cooled by the cooler. In the purification equipment using zinc- or tin-plated carbon steel, dimerization of methyl
15 ethyl ketone may be caused since the plating may be modified due to the high temperature, or the carbon steel inside is precipitated due to peeling or cracking. Therefore, it is preferred that stainless steel be used in a condenser and/or a receiver which is most likely to be in
20 contact with methyl ethyl ketone with a high temperature. As examples of the stainless steel, SUS304, SUS316, SUS405, and SUS410 can preferably be given.

[0013]

As examples of the dimerizing inhibitor material used
25 in the storage equipment, zinc, aluminum, a zinc-aluminum alloy, or tin can preferably be given. It is particularly preferred that the dimerizing inhibitor material be zinc or

aluminum. Methyl ethyl ketone is cooled to normal temperatures after passing through the cooler, and therefore, may not cause the high temperature problems as mentioned above. Therefore, it is preferable to use
5 equipment composed of low-cost materials, for example, equipment obtained by thermally spraying zinc, aluminum or the like onto the surface of carbon steel which is to be in contact with methyl ethyl ketone.

[0014]

10 In the equipment for purification or storage of methyl ethyl ketone of the invention, at least the surface which is to be in contact with methyl ethyl ketone is formed of a dimerizing inhibitor material. As examples of such equipment, equipment formed of stainless steel or
15 equipment formed of carbon steel to which zinc, aluminum or the like is sprayed can be given. Such equipment can be applied in a chemical plant by a known method.

By use of equipment of purifying or storing methyl ethyl ketone of the invention, dimerization of methyl ethyl
20 ketone can be suppressed.

[0015]

As an evaluation example, results of evaluating an increase in the amount of a heavy component when various materials are immersed in methyl ethyl ketone will be
25 explained.

[0016]

Evaluation Method

Various samples were put in a glass-made container together with methyl ethyl ketone (MEK). The glass-made container was then immersed in a constant temperature bath of which the temperature was kept at constant. The content
5 of a heavy component was measured using gas chromatography whenever a predetermined time elapses. In each test, the content of a heavy component of methyl ethyl ketone alone (blank) was also measured.

[0017]

10 Evaluation Example 1

One gram of iron rust collected from an open tank formed of carbon steel and one gram of iron powder obtained by scratching carbon steel without rust were separately put in glass containers and then immersed in 50 ml of methyl
15 ethyl ketone (produced by Idemitsu Kosan, Co., Ltd.). The content of a heavy component generated was measured when the immersion temperatures were 15°C to 50°C. The results obtained are shown in Table 1.

From the results, it was confirmed that iron rust
20 (iron oxide) promotes dimerization of MEK.

[0018]

[Table 1]

Immersion temperature : 15°C			Immersion temperature : 20°C			Immersion temperature : 30°C				Immersion temperature 40°C				Immersion temperature : 50°C			
Time	Blank	Iron rust	Time	Blank	Iron rust	Time	Blank	Iron powder	Iron rust	Time	Blank	Iron powder	Iron rust	Time	Blank	Iron powder	Iron rust
0	40	40	0	34	34	0	43	43	43	0	43	43	43	0	43	43	43
3	38	120	3	32	75	5	43	44	680	5	44	44	1380	4	47	47	1470
20	35	480	5	34	132	24	45	45	1930	24	43	43	3310	22	46	46	3410
25	36	720	25	36	974	28	45	45	2220	28	45	45	3610	26	46	47	3860
71	41	1175	49	36	1470	96	46	46	3980	96	47	47	5600	94	47	51	5200
115	37	1580	74	36	1920	-	-	-	-	-	-	-	-	-	-	-	-
-	-	-	92	38	2140	-	-	-	-	-	-	-	-	-	-	-	-

In the table, the time and the content of a heavy component are expressed as hours and wt
5 ppm, respectively.

[0019]

Evaluation Example 2

Two pieces of zinc-sprayed carbon steel plate (30 mm x 30 mm x 3 mm (thickness), thickness of zinc layer: 80µm: 5 Sample A) and two pieces of plate obtained by subjecting Sample A to a Si-sealing treatment (Sample B) were provided. These samples were immersed in 50 ml of MEK, and the amount of a heavy component generated at an immersion temperature of 30°C or 50°C was measured. The results obtained are 10 shown in Table 2. In each sample, production of a heavy component was suppressed as compared with the case of Evaluation Example 1.

[0020]

Table 2

Immersion time	Immersion temperature : 30°C			Immersion temperature : 50°C		
	Blank	Sample A	Sample B	Blank	Sample A	Sample B
0 hours	50	51	49	48	48	50
1 hour	-	-	-	47	50	47
5 hours	-	-	-	50	61	53
24 hours	51	55	52	49	81	61
48 hours	51	59	56	50	91	68
72 hours	49	61	59	49	94	75
96 hours	52	62	60	49	94	80
147 hours	-	-	-	51	107	96

In the table, the content of a heavy component was expressed as wt ppm.

Sample A: Obtained by thermally spraying zinc to carbon steel

- 5 Sample B: Obtained by coating Sample A with a hydrolyzed alcohol solvent-based silica sol (tetraethylorthosilicate, manufactured by Kanto Chemical Co., Ltd.) for sealing [0021]

Evaluation Example 3

- 10 Each of the following samples (60 mm x 50 mm x 6 mm (thickness)) was immersed in 200 ml of MEK. The amount of a heavy component produced at an immersion temperature of 35°C was measured. The results are shown in Table 3. In each sample, production of a heavy component was suppressed as compared with the case of Evaluation Example 1.

Sample C: Obtained by thermally spraying zinc to carbon steel (zinc thickness: 80 μm)

- Sample D: Obtained by subjecting Sample C to a Zn(OH)₂ sealing treatment (specifically, obtained by subjecting
20 Sample C to a Zn(OH)₂ sealing treatment by rinsing after thermally spraying zinc, followed by drying)

- Sample E: Obtained by subjecting Sample C to an epoxy resin sealing treatment (specifically, obtained by subjecting Sample C to a sealing treatment with a double-fluid epoxy
25 resin which is curable at normal temperatures after thermally spraying zinc)

Sample F: Obtained by thermally spraying a zinc-aluminum

alloy to carbon steel (alloy thickness: 80 μm)

Sample G: Obtained by rinsing and drying after subjecting

Sample F to a $\text{Zn}(\text{OH})_2$, $\text{Al}(\text{OH})_3$ sealing treatment

(specifically, obtained by subjecting Sample F to a $\text{Zn}(\text{OH})_2$,

5 $\text{Al}(\text{OH})_3$ sealing treatment by rinsing after thermally
spraying a zinc-aluminum alloy, followed by drying)

Sample H: Obtained by subjecting Sample F to the same Si
sealing treatment as Sample B.

Sample I: White gas tube (zinc-plated steel pipe)

[0022]

Table 3

Immersion time	Blank	Sample C	Sample D	Sample E	Sample F	Sample G	Sample H	Sample I
78 hours	52	74	85	-	64	96	-	82
98 hours	53	-	-	55	-	-	57	-
123 hours	55	81	95	-	67	100	-	92
175 hours	56	86	103	-	74	107	-	107
198 hours	55	-	-	56	-	-	59	-
248 hours	55	89	104	57	73	111	60	120
320 hours	55	89	102	56	75	111	60	131
417 hours	56	89	104	57	76	113	60	145
533 hours	59	-	-	58	-	-	67	-
721 hours	61	-	-	58	-	-	66	-
845 hours	66	-	-	64	-	-	70	-

In the table, the content of a heavy component is expressed as wt ppm.

[0023]

Evaluation Example 4

Each of the following samples (60 mm x 50 mm x 3 mm (thickness)) was immersed in 200 ml of MEK. The amount of
5 a heavy component produced at an immersion temperature of 35°C was measured. The results obtained are shown in Table 4.

Sample J: Tank iron plate (carbon steel)

Sample K: Obtained by forming a film on carbon steel with
10 zinc-rich paint (Product Name: "SD Zinc 1500A", manufactured by Kansai Paint, Co., Ltd.)

Sample L: Obtained by coating carbon steel with an epoxy resin (Product Name "Million Clear" manufactured by Kansai Paint, Co., Ltd.)

15 [0024]

[Table 4]

Immersion time	Blank	Sample J	Sample K	Sample L
25 hours	53	802	63	48
191 hours	58	968	98	53
312 hours	55	976	101	52
570 hours	54	985	133	49
981 hours	61	987	169	50
1581 hours	156	1096	193	54
2084 hours	172	1206	210	47

In the table, the content of a heavy component is expressed

as wt ppm.

[0025]

From the results, it was confirmed that production of a heavy component was suppressed in Samples K and L.

5 However, in Sample K, alcohols and ketones were detected in addition to an ordinary heavy component after the lapse of 1,000 hours. In the case of the epoxy-resin coated sample, an eluted component of the epoxy resin was detected.

Therefore, Samples K and L are not preferable for use in
10 equipment for producing MEK.

INDUSTRIAL APPLICABILITY

[0026]

By the method for suppressing production of a heavy
15 component of methyl ethyl ketone and the equipment for purification or storage of methyl ethyl ketone of the invention, deterioration in quality of methyl ethyl ketone in purification and during storage can be prevented.

CLAIMS

1. A method for suppressing production of a heavy component of methyl ethyl ketone comprising using a dimerizing inhibitor material at least in a surface of purification or storage equipment which is to be in contact with methyl ethyl ketone.

2. The method for suppressing production of a heavy component of methyl ethyl ketone according to claim 1, wherein the dimerizing inhibitor material is zinc, aluminum, a zinc-aluminum alloy, tin, stainless steel, a fluorine-based resin or a polyolefin resin.

3. The method for suppressing production of a heavy component of methyl ethyl ketone according to claim 2, wherein the dimerizing inhibitor material used in the purification equipment is stainless steel.

4. The method for suppressing production of a heavy component of methyl ethyl ketone according to claim 3, wherein the purification equipment is a condenser which cools methyl ethyl ketone and/or a receiver which temporarily receives methyl ethyl ketone.

5. The method for suppressing production of a heavy component of methyl ethyl ketone according to claim 2,

wherein the dimerizing inhibitor material used in the storage equipment is zinc, aluminum, a zinc-aluminum alloy, or tin.

- 5 6. A purification or storage equipment for methyl ethyl ketone comprising at least a surface to be in contact with methyl ethyl ketone made of a dimerizing inhibitor material.