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(54) **Title:** PROCESS FOR THE PREPARATION OF BUTADIENE FROM BUTENES BY OXIDATIVE DEHYDROGENATION

(57) **Abstract:** A process for the production of a diene by dehydrogenation of an alkene comprises the step of reacting a feed stream containing said alkene over a metal oxide catalyst at a temperature sufficient to effect conversion of said alkene to said diene to form a product stream containing said diene, characterised in that said feed stream comprises said alkene, oxygen, optionally an inert gas and optionally steam, wherein the molar ratio of alkene : O₂ : steam in said feed stream is in the range 1 : 0.5 - 1 : 0 - 5.



PROCESS FOR THE PREPARATION OF BUTADIENE FROM BUTENES BY
OXIDATIVE DEHYDROGENATION

The present application concerns a process for the dehydrogenation of an alkene.

Dehydrogenation of alkenes is known. In particular the manufacture of butadiene by the oxidative dehydrogenation of butene is known. Oxygen is co-fed with the butene-containing feed in order to combine with and remove hydrogen formed in the dehydrogenation to drive conversion of the butene and discourage the reverse (hydrogenation) reaction:



The reaction proceeds in the presence of a catalyst and steam. The oxygen also combines with some of the butene feedstock to provide heat and may also prolong the active life of the catalyst by burning away coke deposits. Commercial processes operate in the presence of added steam, usually present in amounts to produce a molar ratio in the feed stream of at least 10: 1 (steam : hydrocarbon). The steam is used to assist with management of heat in the reactor and to minimise the deactivation of the catalyst by minimising the deposition of carbon onto the catalyst. Whilst all commercial processes use steam, the presence of large volumes of steam brings disadvantages, including the energy requirement involved in generating, pumping and later separating the steam from the reaction products. We have found, surprisingly, that the process may be advantageously operated at very low steam ratios.

According to the invention, a process for the production of a diene by dehydrogenation of an alkene comprises the step of reacting a feed stream containing said alkene over a catalyst bed comprising a metal oxide catalyst at a temperature sufficient to effect conversion of said alkene to said diene to form a product stream containing said diene, said feed stream comprising said alkene, oxygen, optionally an inert gas and optionally steam, wherein the molar ratio of alkene : O₂ : steam in said feed stream is in the range 1 : 0.5 - 1 : 0 - 5.

In this specification, all ratios of steam, alkene and/or oxygen are given as a molar ratio unless otherwise stated.

The process is particularly useful for the production of butadiene from n-butene (1-butene and/or 2-butene). To avoid the cost of separating 1-butene and 2-butene from a mixture of n-butenes, the process may comprise feeding a mixed butenes feed containing 1-butene and 2-butene. The alkene may comprise or consist of n-butenes. The alkene may be n-butene(s) and the diene may be butadiene.

The catalyst is a metal oxide catalyst. Known catalysts for the oxidative dehydrogenation of alkenes include oxides of bismuth, molybdenum, iron, magnesium, manganese, zinc, aluminium, platinum, tin, vanadium, zirconium, beryllium, calcium, strontium and other transition metals such as Cu, Co, and Ni. Most commonly, catalysts based on mixed oxides

of Bi + Mo and on Fe + Mg/Mn are proposed for this reaction. Mixed Bi and Mo oxides include bismuth molybdate catalysts. Bismuth molybdate catalysts may be in the alpha, beta or gamma forms. The catalyst may comprise alpha or beta bismuth molybdate. Other elements, e.g. metals or metal oxides, may be present.

- 5 The catalyst may be made by conventional catalyst manufacturing methods. Suitable methods include precipitation, and may include co-precipitation of more than one compound. The precipitated compounds may be converted to catalytically active or stable compounds by methods including heat treatment.

- 10 The reaction temperature is typically in the range 300 - 600 °C, and may be in the range 350 - 500 °C, especially in the range 400 - 450 °C. The skilled person will adjust the reaction temperature as required in order to maintain a desired rate of conversion of alkene. The dehydrogenation reaction is endothermic, whilst the reaction of oxygen with produced hydrogen is highly exothermic. The presence of oxygen in the feed stream may provide heat by burning a hydrocarbon present in the feed stream. The hydrocarbon may comprise a
15 portion of the alkene feed. An inert gas may be added to the reactor in order to control the reaction temperature. Suitable inert gases include nitrogen, for example. Heat management within the reactor may be carried out as necessary, by heating or cooling at least portions of the reactor. The reaction pressure may be typically in the range from 1 to 10 barg (gauge pressure of 0.1 - 1 MPa).

- 20 Oxygen performs several useful functions in the reaction and is typically co-fed to the reactor with the alkene feed. It is, however, desirable to convert as much of the added O₂ as possible in order to avoid the need to separate O₂ from the gaseous products of the reaction. One advantage of the process of the invention is that the low steam ratios may promote relatively high conversion of oxygen. The alkene : O₂ molar ratio is within the range 1 : 0.5 - 1. The
25 reaction has been found to run well with an alkene : O₂ molar ratio within the range 1 : 0.7 - 0.8, for example about 1: 0.75.

- Operation of the process with alkene: steam molar ratios of 1 : 0 - 5, especially 1: 0 - 3, alleviates the problem of using energy to generate, pump and separate large volumes of steam. We have found an unexpected benefit of using such low steam ratios may be the
30 lower deactivation rate of a bismuth molybdate catalyst compared with the deactivation rate when higher steam ratios are used. Without being bound by theory, we propose that such an effect may be due to the volatilisation of molybdenum which may be accelerated by the presence of steam. Reduced quantities of steam appear to alleviate such effects, with the result that the active catalyst lifetime is improved. We have also found that, contrary to
35 accepted practice, it is not necessary to supply steam to the reaction in order to avoid the formation of carbon on the surface of a catalyst. We have found that it is possible to operate

the process of the invention for at least 140 hours in the absence of steam in the feed without carbon forming on the catalyst.

It is clear from the reaction scheme that water is produced in the process as a result of the reaction between oxygen and hydrogen produced from the dehydrogenation of the alkene. At reaction temperatures, this water is present as steam. When we refer to the steam ratios or to the molar ratio of alkene (e.g. n-butene) : O₂ : H₂O being in the range 1 : 0.5 - 1 : 0 - 5, we refer to steam, or water, present in the feed to the reactor and not to the steam, or water, produced in the reactor as a result of the reaction between oxygen and produced hydrogen. In conventional dehydrogenation processes, steam is added to the reactor, either as steam or as liquid water. When water is added, it is readily vaporised to steam at reaction temperatures. Alternatively steam may be formed in a vaporisation step and added to the reactor in that form. The feed stream comprising alkene, oxygen, optionally an inert gas and optionally steam may be combined as a single feed stream or the components may be added to the reactor separately or as a combination of co-feeding and separate feeding. In a preferred process the ratio of alkene: steam is in the range 1:0 to 3, especially 1: <3, for example 1: 0 - 2 by volume, and 1: 0 – 1.5 by volume, including 0 – 1.0 by volume or 0 – < 1 by volume. The molar ratio of alkene: steam is in the range 1:0 to 3, especially 1: <3, for example 1: 0 - 2, particularly 1: 0 – 1.5, including 0 – 1.0 or 0 – < 1. Under the conditions used, any difference between volume ratio and molar ratio is believed to be immaterial so that molar ratio and volume ratio have the same value.

The reaction may be carried out continuously under fixed bed conditions. The reaction may take place in an axial or a radial flow reactor. The catalyst may be present as a bed of catalyst particles supported within a reactor space, i.e. in a so-called "fixed bed" reactor. The catalyst particles for such reactors are typically pellets, tablets or other "catalyst units" having a minimum dimension of at least 0.5 mm. The catalyst units may be shaped as cylinders, multi-lobed cylinders (e.g. tri-lobes), spheres, rings, saddles or other shapes. A large number of suitable catalyst shapes and sizes for use in catalyst beds are well-known to the skilled catalyst developer and to process operators. The selection of suitable shapes and sizes may be directed by the strength of the catalyst, desired gas flow and heat management within the catalyst bed. The reactor may be provided with means for controlling the reaction temperature, such as heating and/or cooling means or for measuring the temperature at one or more locations within the reactor. The reaction may take place in a non-adiabatic reactor, especially a reactor having a heat transfer medium for heating or cooling. The heat transfer medium may include any suitable conventional type, including oils and molten salt cooling. The reactor may include one or more reactor tubes, for example in a shell and tube reactor. The reaction may alternatively be carried out under fluid bed conditions. A catalyst for fluidised bed operation typically comprises smaller particles than those used in a fixed bed reactor. Fluidised bed processes are particularly beneficial when rapid catalyst deactivation

takes place leading to a requirement for continual catalyst regeneration. A fluidised bed may provide greater opportunity for temperature management of the reaction than a fixed bed reaction, although catalyst particle attrition is a known problem with fluidised bed operation.

The process may be operated at a range of conditions. The process is operated in the gas phase. The gas hourly space velocity (GHSV) may be varied within a wide range of parameters. The GHSV may be from about 300 to about 1500 hr⁻¹. The GHSV is calculated as the volume of alkene fed per hour divided by the volume of catalyst bed. Increasing the space velocity may increase selectivity of the reaction to the desired diene. Increasing the reaction temperature may increase conversion and compensate for any loss of conversion due to increased space velocity.

The products of the reaction are usually processed in at least one separation step, which may comprise a distillation or fractionation. The organic components of the product stream, comprising unreacted alkene and product diene are separated. The product diene, optionally after further purification steps may be stored or used directly in a subsequent process.

Unreacted alkene may be recycled to the dehydrogenation reaction. Steam or water may be separated from the product stream and a portion of it may be recycled to the dehydrogenation reaction if desired, although it is a particular feature of the process of the invention that the reaction takes place in the presence of low steam volumes or no steam, so that the amount of cooling required to separate steam or water from the product stream is much reduced. The process flow sheet includes such other steps as may be conventionally carried out for such a process. Such steps may include, mixing, vaporisation, heating, cooling, purification, effluent treatment etc.

The process will be further described in the following Examples, which are not to be deemed as limiting the scope of the invention.

Example 1: Preparation of beta bismuth molybdenum oxide Bi₂Mo₂O₉

Ammonium paramolybdate (7.04g, 0.0057 mols) was dissolved in de-ionised water (200 ml). Concentrated nitric acid was added dropwise to lower the pH to 1.8 and the solution was aged for 15 minutes. Bismuth nitrate (19.4g, 0.039mols) was dissolved in a mixture of concentrated nitric acid (15 ml) and water (30 ml). The bismuth nitrate solution was added over a period of 30 minutes to the aged molybdenum solution whilst maintaining a pH 1.8 using concentrated ammonia. The resulting suspension was filtered, air dried at room temperature (16 hours) followed by a heat treatment at 115°C (5°C per min, hold for 1 hour), then 200°C (5 °C per min, hold 3 hours), then 450°C (5°C per min, hold 3 hour). A pale yellow solid was obtained. The resulting solid material was characterised using X-ray diffraction (XRD), Raman spectroscopy and X-ray fluorescence spectroscopy (XRF) to confirm the identity of the product as β-bismuth molybdate (Bi₂Mo₂O₉).

Example 2: Preparation of gamma bismuth molybdenum oxide Bi_2MoO_6

Ammonium paramolybdate (10.58g, 8.56mols) was dissolved in de-ionised water (140ml). Bismuth nitrate (58.28g, 0.120mols) was dissolved in a mixture of concentrated nitric acid (15 ml) and water (30 ml). The bismuth nitrate solution was added over 30 minutes to the aged molybdenum solution whilst maintaining a pH of 2 using 28 wt% ammonia. The resulting suspension was filtered, air dried at room temperature (16 hours) followed by a heat treatment at 115°C (5°C per min, hold for 1 hour), then 200°C (5 °C per min, hold 3 hours), then 450°C (5°C per min, hold 3 hours). A pale yellow solid was obtained, which was characterised using X-ray diffraction (XRD), Raman spectroscopy and X-ray fluorescence spectroscopy (XRF) to confirm the identity of the product as γ -bismuth molybdate (Bi_2MoO_6).

Example 3: Preparation of alpha bismuth molybdenum oxide $\text{Bi}_2\text{Mo}_3\text{O}_{12}$

Ammonium paramolybdate (128.53g, 0.104 mols) was dissolved in de-ionised water (1600 ml). Concentrated nitric acid was added dropwise to pH 1.5 and the solution aged for 1 hour. Bismuth nitrate (232.83g 0.480mols) was dissolved in a mixture of concentrated nitric acid (140 ml) and water (500 ml). The bismuth nitrate solution was added over 30 minutes to the aged molybdenum solution whilst maintaining a pH 1.5 using concentrated ammonia. The resulting suspension was aged for 1 hour, filtered, air dried at room temperature (16 h) followed by a heat treatment at 115 °C (5°C per min, hold for 1 hour), 200°C (5 °C per min, hold for 3 hours), 450°C (5°C per min, hold for 3 hours). A pale yellow solid was obtained, which was characterised using X-ray diffraction (XRD), Raman spectroscopy and X-ray fluorescence spectroscopy (XRF) to confirm the identity of the product as α -bismuth molybdate ($\text{Bi}_2\text{Mo}_3\text{O}_{12}$).

The solid α -bismuth molybdate catalyst was formed into 3.3 mm pellets using 1 wt% graphite as lubricant. The pellets were then ground and sieved to 1.7 to 2 mm fractions before testing for activity.

Catalyst Testing

Alpha- $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ (2.8ml, 5.4g, particle size between 1.7 and 2 mm) was mixed with silicon carbide (3.2g, particle size between 300 and 600 μm). A fixed bed reactor (19 mm diameter) was charged with the catalyst and silicon carbide mixture. Silicon carbide (3g, particle size between 300 and 600 μm) and alumina rocks are charged on top of the reactor. The reactor is connected to the testing rig. A flow of 10%(by volume) O_2 in N_2 was passed over the catalyst at 210 ml/min (1 barg). The temperature of the reactor was raised to 470°C and then the temperature was maintained for 1 hour before the temperature was reduced to 440°C. 1-butene (pure grade) was introduced (flow 30 ml/min) together with steam at steam to butene volume ratio of 10 to 1 and 5 to 1. Experiments were also performed with no steam added to the gas feed. The reaction mixture was continuously analysed by on-line gas chromatography (GC).

The butene to O₂ ratio and space velocities were varied between experiments, as indicated in the results tables. O₂/N₂ flows and catalyst volumes were adjusted for the new conditions.

For on-line GC, butenes and butadiene are analysed on a flame ionisation detector using the following column: plot fused silica 50 m x 0.53 mm, coating Al₂O₃/Na₂SO₄, DF = 10 µm.

- 5 Helium at a flow of 30 ml/min is used as carrier gas.

CO, CO₂ and O₂ are analysed using a thermal conductivity detector using a HayeSep® column and a Molecular Sieve 13X column in series. Helium at a flow of 30 ml/min is used as carrier gas.

GHSV, Gas Hourly Space Velocity = (Volume of butene fed per hour/ Volume of catalyst)

- 10 Butenes conversion (%) =
$$\frac{\text{(Amount butene fed - total amount butenes in exit stream)}}{\text{(amount of butene fed)}} \times 100$$

Yield (%) =
$$\frac{\text{(Amount of product in the exit stream)}}{\text{(amount of butene fed)}} \times 100$$

- 15 Selectivity (%) =
$$\frac{\text{Yield of product}}{\text{Butenes conversion}} \times 100$$

Table 1 shows results using α-Bi₂Mo₃O₁₂, as described in Example 3, as catalyst at a reaction temperature of 440°C, GHSV 640h⁻¹, butene : O₂ volume ratio 1 : 0.7, steam : butene volume ratio as stated in the table. In the table, the column labelled "A" shows the averaged results for the first five hours on-line and column "B" shows the averaged results obtained between 85 and 90 hours on-line operation of the process.

Table 1

Steam : butene ratio	Butenes Conversion (%)		Butadiene yield (%)		Butadiene selectivity (%)		CO + CO ₂ yield (%)		O ₂ conversion (%)	
	A	B	A	B	A	B	A	B	A	B
10 : 1	64.8	58.8	53.3	50.7	86.6	86.3	7.4	4.5	98.6	71.9
5 : 1	65.9	64.3	57.4	57.3	87.1	89.1	7.5	6.3	96.6	91.5
No steam	74	73.2	64.1	63.2	82.3	86.3	7.5	6.9	99.8	100

- 25 Table 2 shows results using α-Bi₂Mo₃O₁₂ as catalyst at a reaction temperature of 440°C, with GHSV and butene : O₂ volume ratio as shown in the table, and no steam. In the table, the column labelled "A" shows the averaged results for the first five hours on-line and column "B" shows the averaged results obtained between 85 and 90 hours on-line operation of the process.

Table 3 shows results using α -Bi₂Mo₃O₁₂, β -Bi₂Mo₂O₉ and γ -Bi₂MoO₆ as catalyst at a reaction temperature of 440°C, GHSV 640h⁻¹, butene to O₂ volume ratio 1 to 0.7, in the absence of steam. The reactions were carried out using the general method described for the alpha catalyst above. The β -Bi₂Mo₂O₉ and γ -Bi₂MoO₆ catalyst particles were obtained by grinding and sieving the material after the heat treatment, without a pelleting step. In the table, the column labelled "A" shows the averaged results for the first five hours on-line and column "B" shows the averaged results obtained between 85 and 90 hours on-line operation of the process, with the exception of γ -Bi₂MoO₆ for which the column B results represent average results between 60 and 65 hours online, due to deactivation.

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Table 2

O ₂ : butene ratio	GHSV (h ⁻¹)	Butenes Conversion (%)		Butadiene yield (%)		Butadiene selectivity (%)		CO + CO ₂ yield (%)		O ₂ conversion (%)	
		A	B	A	B	A	B	A	B	A	B
0.7	640	74	73.2	64.1	63.2	82.3	86.3	7.5	6.9	99.8	100
0.8	640	78.9	78.9	66.5	68.4	84.3	86.7	9.7	9.6	99.5	99.5
0.8	900	75.3	74.4	68.2	69.1	90.5	92.9	8.6	8.5	99.3	98.3

Table 3

Catalyst	Butenes Conversion (%)		Butadiene yield (%)		Butadiene selectivity (%)		CO + CO ₂ yield (%)		O ₂ conversion (%)	
	A	B	A	B	A	B	A	B	A	B
α -Bi ₂ Mo ₃ O ₁₂	74	73.2	64.1	63.2	82.3	86.3	7.5	6.9	99.8	100
β -Bi ₂ Mo ₂ O ₉	83	77.6	76.1	72.8	91.6	93.8	6	6.1	99.4	99.4
γ -Bi ₂ MoO ₆	84.1	55.1	72.7	41.1	86.4	74.7	8	11.3	99.4	99.7

The rate of deactivation was calculated for each catalyst under the operating conditions shown in Table 4. The rate of deactivation is indicated in Table 4 as the change in butadiene yield per hour between 10 and 90 hours on line. This shows that the γ -Bi₂MoO₆ exhibits a high rate of deactivation under the process conditions used.

15

Table 4

Butene : O ₂ : water	GHSV (h ⁻¹)	Catalyst	Change in hourly butadiene yield (% BD yield.h ⁻¹)
1 : 0.7 : 10	640	α -Bi ₂ Mo ₃ O ₁₂	-0.04
1 : 0.7 : 5	640	α -Bi ₂ Mo ₃ O ₁₂	-0.02
1 : 0.7 : 0	640	α -Bi ₂ Mo ₃ O ₁₂	-0.02
1 : 0.7 : 0	640	β -Bi ₂ Mo ₂ O ₉	-0.03
1 : 0.7 : 0	640	γ -Bi ₂ MoO ₆	-0.65

α -Bi₂Mo₃O₁₂ catalysts were analysed by thermal gravimetric analysis (TGA) after the reaction to measure the amount of carbon present. Results are reported in Table 5.

Table 5: TGA analyses of the fresh and used catalysts

	Carbon content (weight %)
Fresh catalyst	1.1
Steam : butene ratio	
No steam	0.8
5 : 1	1.1
10 : 1	0.95

Example 4

- 5 An oxidative dehydrogenation process was operated as described above at GHSV 1400 hr⁻¹, a reaction temperature of 370°C and a volume ratio of butene : O₂ of 1: 0.6. The catalyst used was an oxidic catalyst containing bismuth, molybdenum, iron and cobalt in the form of particles having an average size in the range 1 – 1.7 mm.

- The initial ratio of butene : steam in the gas feed to the reactor was 1:5 by volume. After
 10 about 23 hours the ratio was changed to 1:4. After a total of about 42 hours online, the butene to steam ratio was changed to 1 : 3. The yield of butadiene was calculated as shown above. The rate of change of butadiene yield with time was calculated from the slope of the curve for butadiene yield at each value of butene : steam ratio in order to demonstrate how each set of conditions affected the rate of deactivation of the catalyst. The results are
 15 shown in Table 6.

Table 6

Volume ratio butene : steam in feed	Rate of change of butadiene yield with time (% yield variation per hour)
1: 5	-0.1486
1: 4	-0.0329
1: 3	-0.0108

- The results demonstrate that reducing the amount of steam present (as a ratio to 1-butene) decreases the rate of deactivation of the catalyst (expressed as % yield variation per hour). The rate of change of yield is negative in each case, indicating that the yield is decreasing,
 20 but the rate of change is much less at lower steam ratios.

Example 5

An oxidative dehydrogenation process was operated as described above using α -Bi₂Mo₃O₁₂ as catalyst at GHSV 2000 hr⁻¹, a reaction temperature of 380 °C and a volume ratio of butene: O₂ of 1: 0.6. The initial volume ratio of butene : steam in the gas feed to the reactor was 1:10.

After about 16 hours the ratio was changed to 1 : 1. After a total of about 32 hours online, the butene to steam ratio was changed to 1 : 0.5. The results are shown in Table 7.

Table 7

Butene : steam ratio	Butenes Conversion (%)	Butadiene selectivity (%)	Butadiene yield (%)
1 : 10	64.91	40.44	26.14
1 : 1	55.25	61.74	34.12
1 : 0.5	51.42	66.98	34.43

Claims

1. A process for the production of a diene by dehydrogenation of an alkene comprising the step of reacting a feed stream containing said alkene over a metal oxide catalyst at a temperature sufficient to effect conversion of said alkene to said diene to form a product stream containing said diene, characterised in that said feed stream comprises said alkene, oxygen, optionally an inert gas and optionally steam, wherein the molar ratio of alkene : O₂ : steam in said feed stream is in the range 1 : 0.5 - 1 : 0 - 5.
2. A process as claimed in claim 1, wherein said catalyst comprises at least one oxide of a metal selected from the group consisting of bismuth, molybdenum, iron, magnesium, manganese, zinc, aluminium, platinum, tin, vanadium, zirconium, beryllium, calcium, strontium, copper, cobalt and nickel.
3. A process as claimed in claim 1 or claim 2, wherein said reaction temperature is in the range 300 - 600 °C.
4. A process as claimed in any one of the preceding claims, wherein the molar ratio of alkene : O₂ is in the range 1 : 0.7 - 0.8.
5. A process as claimed in any one of the preceding claims, wherein gas hourly space velocity (GHSV) is from about 300 to about 1500 hr⁻¹.
6. A process as claimed in any one of the preceding claims wherein the molar ratio of alkene : O₂ : steam in said feed stream is in the range 1 : 0.5 - 1 : 0 - 3.
7. A process as claimed in claim 6 wherein the molar ratio of alkene : O₂ : steam in said feed stream is in the range 1 : 0.5 - 1 : 0 - 2
8. A process as claimed in any one of the preceding claims, wherein no H₂O is added to the reaction.
9. A process as claimed in any one of the preceding claims, wherein said catalyst comprises a bed of catalyst particles.
10. A process as claimed in any one of the preceding claims, wherein said alkene comprises n-butene and said diene comprises butadiene.
11. A process as claimed in claim 10, wherein said alkene comprises 1-butene and 2-butene.

INTERNATIONAL SEARCH REPORT

International application No
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A. CLASSIFICATION OF SUBJECT MATTER

INV. C07C5/48 B01J37/03 B01J23/38
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 B01J

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X A	DE 10 2013 226370 A1 (EVONIK INDUSTRIES AG [DE]) 18 June 2015 (2015-06-18) Examples; page 24 - page 26 -----	1-7,9-11 8
X A	EP 2 862 626 A1 (LG CHEMICAL LTD [KR]) 22 April 2015 (2015-04-22) Application example -----	1-7,9-11 8
X A	US 2014/163292 A1 (GRÜNE PHILIPP [DE] ET AL) 12 June 2014 (2014-06-12) paragraph [0186]; examples 3-5 -----	1-7,10, 11 8



Further documents are listed in the continuation of Box C.



See patent family annex.

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