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(71) Applicant *(for all designated States except US)*: **BP CHEMICALS LIMITED** [GB/GB]; Britannic House, 1 Finsbury Circus, London EC2M 7BA (GB).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: **GRACEY, Patrick, Benjamin** [GB/GB]; 5 Anson Villas, Paull, Hull HU12 8AJ (GB). **HAZEL, Nicholas, John** [GB/GB]; 31 Danesway, Beverley, East Yorkshire HU17 7JQ (GB).

(74) Agent: **HYMERS, Ronald, Robson**; BP International Limited, Patents & Agreements, Chertsey Road, Sunbury on Thames, Middlesex TW16 7LN (GB).

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(54) Title: PROCESS FOR THE PRODUCTION OF ACETIC ACID C4-ESTERS

(57) Abstract: Process for treating a mixed C_4 stream comprising iso-butene and 1,3-butadiene by (a) reacting the stream with acetic acid in an addition reactor, (b) withdrawing product comprising iso-butene, sec-butenyl acetate, n-butenyl acetate and t-butyl acetate, and recovering n-butenyl acetate from the product and separating and recycling t-butyl acetate to the addition reactor. The process provides increased efficiency of acetic acid utilisation together with useful products, *e.g.* n-butenyl and sec-butenyl acetates which can be separated and sold as such or converted to other products. The unreacted isobutene can be separated and used as such, or recycled and allowed to dimerise to di-isobutene, another useful product.

PROCESS FOR THE PRODUCTION OF ACETIC ACID C4-ESTERS

This invention relates to a process for treating a mixed C_4 stream comprising iso-butene and 1, 3- butadiene.

In naphtha steam-cracking, naphtha is decomposed in the presence of a steam diluent at a temperature between 700 and 900°C. The process produces a number of products, including isomeric butanes, 1,3-butadiene and isomeric butenes (e.g. 1-butene, 2-butene and iso-butene). These compounds may be separated as a mixed C_4 stream.

As described in WO 00/26175, mixed C_4 streams may be contacted with acetic acid in the presence of a catalyst. Under the reaction conditions, butadiene in the C_4 stream reacts with acetic acid to produce n-butenyl and sec-butenyl acetate. The sec-isomer may be recycled to the reactor. The n-isomer, on the other hand, is recovered and hydrogenated to produce n-butyl acetate which is a useful solvent.

Not all the acetic acid initially fed to the reactor is consumed in the butadiene/acetic acid addition reaction. Instead, some of the acetic acid reacts with the iso-butene present in the mixed C_4 feedstock to produce t-butyl acetate. This by-product is isolated from the product mixture and cracked back to iso-butene and acetic acid. The iso-butene is recovered by distillation, and sold, for example, as a feedstock for the production of polyisobutene (PIB). The acetic acid is recycled to the reactor, and may be re-consumed in one of the addition reactions occurring therein.

The cracking and distillation equipment required in the process of WO 00/26175 can add cost and complexity to the overall process. It is therefore among the objects of the present invention to provide an alternative process for treating such mixed C_4 streams.

According to the present invention, there is provided a process for treating a mixed C_4 stream comprising iso-butene and 1,3-butadiene, said process comprising:

a) reacting acetic acid with said stream in an addition reactor,

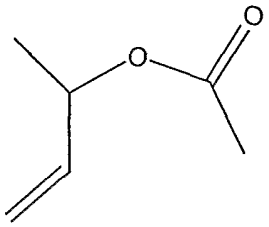
b) withdrawing from the addition reactor a product stream comprising iso-butene, sec-butenyl acetate, n-butenyl acetate and t-butyl acetate, and

c) recovering n-butenyl acetate from the product stream, characterised in that

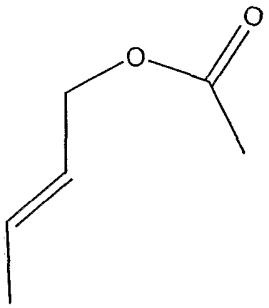
d) t-butyl acetate is recycled to said addition reactor.

For the avoidance of doubt, sec-butenyl acetate and n-butenyl acetate have the following structures:

sec-butenyl acetate



n-butenyl acetate



Under the operating conditions of the addition reactor, isobutene and acetic acid react together reversibly to form t-butyl acetate and hence under stable operating conditions isobutene, acetic acid and tertiarybutyl acetate are substantially in equilibrium. Thus, by recycling the t-butyl acetate back to the reactor, the amount of t-butyl acetate in the reaction loop eventually approaches a substantially constant value. By controlling the amount of t-butyl acetate produced in this manner, the amount of

acetic acid consumed in the reaction between iso-butene and acetic acid is maintained at a substantially constant level. This leaves a significant proportion of the initial acetic acid feedstock available for desirable reactions, such as the addition reaction with 1,3-butadiene. Although in the present invention iso-butene is preferably not produced by cracking t-butyl acetate as described in WO 00/26175, any unreacted iso-butene present in the original mixed C_4 stream may be recovered, for example, by distillation or flash separation techniques.

The mixed C_4 stream employed as a feedstock in the present process can be, for example, a by-product of a reaction, such as the dehydrogenation of butane or butene, or the steam cracking of naphtha. Such mixed C_4 streams frequently comprise isobutene and 1,3-butadiene. The mixed C_4 stream may also comprise one or more of isobutane, n-butane, 1-butene, trans-2-butene, cis-2-butene, 1,2-butadiene, propadiene, methyl acetylene, ethyl acetylene, dimethyl acetylene, vinyl acetylene, diacetylene, and C_5 acetylenes. In one embodiment of the present invention, the mixed C_4 stream is a by-product of naphtha steam cracking comprising isobutane (e.g. 1 - 2 %v/v), n-butane (e.g. 2 - 4%v/v), isobutene (e.g. 25 - 29%v/v), 1-butene (e.g. 8 - 10%v/v), trans-2-butene (e.g. 6 - 8%v/v), cis-2-butene (e.g. 3 - 5%v/v), 1,3-butadiene (e.g. 43 - 48%v/v), 1,2-butadiene (e.g. 0 - 2%v/v), propadiene (e.g. 0 - 1%v/v), methyl acetylene (e.g. 0 - 1%v/v), ethyl acetylene (e.g. 0 - 1%v/v), dimethyl acetylene (e.g. 0 - 1%v/v), vinyl acetylene (e.g. 0 - 1%v/v), diacetylene (e.g. 0 - trace) and C_5 acetylenes (e.g. 0 - trace). It should be understood that the precise composition of the latter stream may vary depending on factors such as the naphtha feed composition and the how the cracker is operated.

As described in step a), the mixed C_4 stream is reacted with acetic acid in an addition reactor. The reaction conditions employed in the addition step are described in detail in WO 00/26175. The relative mole ratios of butadiene in the mixed C_4 stream to acetic acid may be 5:1 to 1:50, preferably, 1:1 to 1:10.

The addition reaction may be carried out at a temperature of 20 to 140°C, preferably, of 40 to 90°C. The reaction may be carried out using a homogeneous or heterogeneous catalyst, the latter being preferred. Suitable catalysts include acidic catalysts such as zeolites, and strong acid ion-exchange resins. Suitable ion-exchange resins include Amberlyst 15® and Amberlite IR120®. A proportion of the acidic sites of

such resins may be exchanged with bulky counterions such as alkyl pyridinium, quaternary alkyl ammonium, quaternary arsonium and quaternary phosphonium compounds. Tetra-phenylphosphonium counterions, for example, may be employed. These counterions may account for up to 10% of the available acidic sites.

Water may be present in the addition step in an amount between 0.05 and 50 % w/w, preferably, 0.5 and 20 w/w %, based on the total charge to the reactor.

In certain cases, the activity of heterogeneous catalysts may decrease after prolonged use. This may be due to blockage of active sites by 1,3-butadiene oligo- and polymerisation products. In such cases, it may be advantageous to carry out the addition reaction under conditions of high shear, as high shear rates are believed to reduce blockage of active sites by the formation of such oligo- and polymerisation products. Alternatively or additionally, polymerisation inhibitors may be added to the reaction mixture. Such inhibitors are well known in the art. Where oligo- and polymerisation products are present in the product stream, however, these may be recovered and recycled to the reactor.

The addition reaction may be carried out using any suitable reactor. For example, a fixed bed, slurry, trickle bed, bus loop, or fluidised bed reactor may be employed.

The reaction between the mixed C_4 stream and acetic acid produces a product stream, which is withdrawn from the addition reactor in step b). This product stream comprises addition products including, *inter alia*, n-butenyl acetate, sec-butenyl acetate and t-butyl acetate. Preferably, such addition products account for 1 to 99%w/w, for example, 5 to 50%w/w of the product stream. The n-butenyl and sec-butenyl acetates result from the addition of acetic acid to butadiene, whilst the t-butyl acetate results from the reaction between acetic acid and iso-butene. Such addition reactions, however, do not generally go to completion and are controlled by a number of factors including how the reaction is conducted (e.g. LHSV), reaction kinetics and equilibrium constants. For this reason, unreacted isobutene and, optionally, unreacted 1,3- butadiene are also present in the product stream. These unreacted C_4 components are relatively volatile, and may be separated, for example, by gas disengagement using any suitable separation unit, such as a flash drum. During such a separation step, other volatile C_4 components in the product stream, such as unreacted isomeric butanes, 1-butene and 2-butene may also be separated. Where butadiene is present in the separated mixture, the separated

mixture may be selectively hydrogenated. This selective hydrogenation step predominantly converts butadiene to 1-butene. Additionally, some isomerisation to 2-butene can occur, as well as further hydrogenation to butane.

The separated mixture of unreacted C_4 components may be used as a feedstock, for example, for alkylation, or for steam cracking. Alternatively, the mixture of unreacted C_4 components may be separated (e.g. by physical and/or chemical methods) into one or more components for sale or use. Isobutene, for example, may be recovered and polymerised to produce polyisobutene (PIB). 1-Butene and/or 2-butene may be separated, for example, as a mixture and used as a fuel additive.

In addition to the compounds mentioned above, the product stream may also comprise polymerisation by-products such as C_8 olefins (e.g. di-isobutene from isobutene) octatrienes (e.g. from butadiene + butadiene) and octadienes (e.g. from butadiene and isobutene), C_{12} olefins (e.g. from vinyl cyclohexene + butadiene, or C_8 olefin + butadiene), C_8 acetates , C_{12} acetates and higher oligomeric materials. It may be desirable to remove one or more of such components from the product stream, for example, by distillation. Di-isobutene recovered from the product stream can, if desired, be converted by hydrogenation to iso-octane, a valuable fuel additive.

In step c), n-butenyl acetate is recovered from the product stream. This may be carried out using any suitable separating unit, for example, one or more distillation columns. An example of a suitable apparatus for performing such separation steps is described in WO 00/26175, particularly with reference to Figure 2 of that document. The full disclosure of WO 00/26175 is incorporated herein by reference. Once recovered, the n-butenyl acetate may be, if desired, cracked back to butadiene and acetic acid, or recycled to the reactor. Where the n-butenyl acetate is cracked back to butadiene and acetic acid, at least one of these components may be recycled to the reactor.

Preferably the recovered n-butenyl acetate is hydrogenated to produce butyl acetate. The hydrogenation may be, for example, carried out under heterogeneous conditions over any suitable catalyst. Examples of suitable catalysts include ruthenium, platinum, nickel (e.g. Raney nickel) and palladium. These metals may be employed as elemental metals or metal compounds. Although unsupported catalysts may be employed, it is preferable to use catalysts supported on inert carriers, such as carbon or

siliceous supports. Preferred catalysts include supported Raney nickels, and ruthenium on carbon.

The hydrogenation may, for example, be carried out at 20 to 250 °C, preferably, 40 to 200 °C. The hydrogenation maybe, for example, carried at a pressure of 1 to 100 barg, preferably, 5 to 50 barg. The hydrogenation can be carried out, for example, in slurry and/or flow reactors.

As described in step d), t-butyl acetate is recovered from the product stream and recycled to the reactor. The recovery step may be carried out using any suitable separating unit, for example, a distillation column. The recovered t-butyl acetate stream may also contain other reaction products and/or unreacted reactants including, for example, water and unreacted C_4 compounds.

Optionally, sec-butenyl acetate may be recovered from the product stream. The separated sec-butenyl acetate may be recycled to the reactor, or isolated for, for example, sale, direct use (eg as a solvent), or further processing. In one embodiment of the invention, the sec-butenyl acetate is thermally cracked back to butadiene and acetic acid. One or both of these starting materials may be recycled to the reactor, or sold as such.

As described above, t-butyl acetate, n-butenyl acetate and sec-butenyl acetate are recoverable from the product stream. This may be achieved by conventional methods, for example, by distillation. In certain cases, however, the components of the product stream have relatively similar boiling points. This may make conventional distillation difficult.

In a preferred embodiment, components of the product stream comprising t-butyl acetate, n-butenyl acetate and sec-butenyl acetate may be separated from said product stream by azeotropic separative methods, for example using an azeotroping column. This technique involves, for example, introducing the product stream into an azeotroping column in the presence of water. Under these conditions, it is possible to form water/t-butyl acetate/n-butenyl acetate/sec-butenyl azeotrope(s). The azeotrope may be recovered as a process stream, preferably, from an upper portion of the azeotroping column, more preferably, as an overhead stream. When this process stream is allowed to settle, the organic components of the azeotrope, namely, t-butyl acetate, n-butenyl acetate and sec-butenyl may form a layer separate from the water and may be

decanted therefrom.

Any residual water may be removed from the decanted mixture by drying the mixture further, for example, using molecular sieve treatment or azeotropic drying. If desired, the azeotroping technique can be adapted by employing an organic azeotroping agent, for example, cyclohexane. Water separated in this manner may be recycled to the azeotroping column. The mixture of t-butyl acetate, n-butenyl acetate and sec-butenyl may then be conveniently separated by conventional distillation techniques. If desired, mixtures of t-butyl acetate and sec-butenyl acetate can be recycled to the reactor thus rendering their separation from one another unnecessary.

A stream comprising unreacted acetic acid and optionally, water and/or reaction by-products may be recovered from the base of the azeotroping column. This stream may be recycled to the reactor. It may be desirable to purify such streams prior to the recycling step, particularly, when tars are present. This may be achieved by introducing the stream into a settling tank, and allowing the tars to separate from the remainder of the stream as a separate phase. This settling step may be facilitated by the addition of water.

It should be understood that the azeotropic distillation procedure described above may be applied to any process stream comprising t-butyl acetate, n-butenyl acetate and sec-butenyl acetate.

The invention is illustrated by reference to the following Tests which show how the composition of a C4 stream changes when subjected to treatment with acetic acid in an addition reactor, but without removal and recycle of the products. Hence the Tests illustrate the build-up of by-products, some of which are valuable materials in their own right (e.g. di-isobutene) and some which are regarded of a lesser utility which would be removed at intervals from a commercial process to prevent undue build-up of involatile by-products.

Tests 1 and 2 – Reaction of acetic acid with a crude C4 stream

To 2699g acetic acid and 28g water was added decane (65g - to act as an internal standard for subsequent Gas chromatographic analysis), and butylated hydroxytoluene (2.4g - polymerization inhibitor). The mixture was charged to a 7.5l stainless steel Parr autoclave containing a cooling coil, and supplied with electric band heaters and internal control thermocouple. The catalyst employed was a proprietary sulphonic acid ion

exchange resin held captive inside a stainless steel mesh bag fixed around the cooling coil. The action of the agitator enables liquid flow through the catalyst "bed". The vessel was sealed and pressure purged with nitrogen several times (to 10 barg), to remove air. The mixture was then heated with agitation at 1000rpm to 60 degrees C (Test 1) nad repeated at 70°C (Test 2). Once at temperature, some 886g of crude C4 was added to the vessel under nitrogen overpressure. Excess nitrogen was used to increase pressure to desired 40 barg. This gave an acetic acid to butadiene ratio of 4.34:1.

The composition of the crude C4 stream is given in Table 1 below.

Reaction time zero was taken as the moment of C4 addition, and the mixture was maintained at the stated temperature for a period of 4 days while liquid samples were periodically withdrawn and analysed by gas chromatography. The results showed a kinetic profile of product mixture; tertiary-butyl acetate, secondary butenyl acetate and crotyl acetate main products, with lesser amounts of tertiary butanol, C8 olefins and acetates, C12 olefins, 4-vinylcyclohexane and oligomer by-products, together with unreacted butadiene and acetic acid.

Table 2, below, shows the product composition (analysis by gas chromatography) from Test 1.

For Test 2 (carried out at 70°C) using the same composition, results are given in Table 3, below.

It can be seen from these static Tests that tertiary butyl acetate forms rapidly under the reaction conditions. It is thus apparent that under suitable working conditions for treating C4 streams in accordance with the present invention, the tertiary butyl acetate can be recycled to an addition reaction, optionally together with other products which may not be desired reaction products. It is also apparent that under the static conditions of Tests 1 and 2 that, after reaching a peak, the concentration of tertiary butyl acetate gradually diminishes. It is believed that this is due to the formation of dimeric or other products either from the tertiary butyl acetate itself or from the isobutene with which it is in equilibrium. It can also be seen from the Tests that, in addition to such useful products as, for example, secondary butenyl acetate and crotyl acetate (which are easily separable from the starting materials), there is a gradual build-up of some other products, e.g., C8 butadiene dimers, C8 acetates and C12 butadiene trimers which are

also useful isolable products.

Table 1: Composition of Crude C4 stream obtained from Naptha cracker	
Component	Percent (weight)
Butadiene	63.2
Butene-1	11.1
Butene-2	6.9
C3's	0.1
C5's	0.015
Isobutane	1.9
Isobutene	5.7
N-Butane	8.9
Total accounted for	97.815

Table 2: Product composition profile obtained at 60°C

Time (mins)	C8 BD dimers	C8 acetates	C12 BD trimers	Oligo-mers	t-BuOAc	Sec-BuOAc	Crotyl acetate	4VCH	t-BuOH
0	0.32	0.03	0.03	0.01	3.99	1.34	2.07	0.00	9.41
29	0.55	0.05	0.07	0.01	113.14	5.25	3.35	0.06	44.04
64	1.25	0.27	0.23	0.02	209.38	15.84	9.19	0.06	74.01
93	2.16	0.43	0.45	0.03	208.85	25.33	15.14	0.08	74.54
142	2.92	0.74	0.71	0.04	203.24	37.26	23.07	0.11	72.73
202	3.12	1.20	1.14	0.10	193.07	50.94	32.51	0.17	69.93
269	3.70	1.65	1.55	0.23	180.62	64.80	43.12	0.20	67.37
322	4.17	2.11	1.99	0.45	169.08	75.83	52.79	0.25	64.74
425	4.65	2.69	2.53	0.78	157.52	89.71	64.66	0.31	62.17
1369	7.31	5.21	5.67	3.98	102.14	155.93	140.23	0.84	48.82
1515	7.50	8.34	6.39	4.80	91.69	167.49	154.81	0.92	45.92
1645	8.07	8.86	6.68	5.23	87.95	171.96	161.12	1.01	44.74
1740	8.28	6.56	6.82	5.40	85.32	174.08	164.92	1.03	43.96
2803	9.79	8.16	7.83	7.23	68.96	185.73	183.16	1.34	38.40
2966	10.19	11.81	8.14	7.66	64.96	186.57	187.96	1.40	37.03
3326	10.61	9.03	8.37	8.23	60.94	186.65	189.67	1.45	35.53
4292	11.48	9.74	8.74	9.44	53.40	185.73	188.66	1.59	32.45
4464	11.79	10.07	8.94	9.82	50.97	183.80	188.66	1.62	31.56
4614	11.91	13.64	8.98	9.44	50.08	184.25	186.96	1.62	31.17
4759	12.08	13.63	8.94	9.26	49.27	184.86	186.59	1.65	30.89
5692	12.59	14.33	9.28	10.11	43.77	176.20	182.88	1.65	28.43
5816	12.86	14.55	9.40	10.50	42.56	176.04	180.45	1.68	27.90
5928	12.91	14.56	9.36	11.24	41.95	175.12	169.92	1.68	27.65

Table 3: Product composition profile obtained at 70°C

Time (mins)	C8 BD dimers	C8 acetates	C12 BD trimers	Oligo-mers	t-BuOAC	sec BuOAc	Crotyl acetate	4VCH	t-BuOH
0	0.12	0.05	0.06	0.01	1.83	1.29	1.52	0.00	2.64
12	0.39	0.10	0.05	0.10	122.36	4.36	3.04	0.08	45.02
25	0.91	0.06	0.14	0.10	195.98	11.70	6.78	0.14	58.69
36	1.24	0.08	0.28	0.10	203.69	18.22	10.57	0.14	58.47
60	1.84	0.45	0.61	0.12	195.05	30.60	18.56	0.17	55.96
117	3.10	1.15	1.36	0.23	173.51	55.88	36.28	0.22	52.14
149	3.66	1.61	1.77	0.38	161.98	68.70	46.49	0.25	49.75
176	4.56	2.49	2.79	1.06	141.45	92.44	67.01	0.31	46.06
307	5.45	3.61	3.99	1.85	120.45	117.69	92.52	0.37	41.76
1312	8.93	6.94	7.57	5.75	70.92	170.84	158.47	0.62	29.67
1434	16.20	7.80	8.38	6.58	61.98	177.00	169.52	0.65	27.11
1711	10.96	8.20	8.85	7.60	56.36	177.79	172.44	0.67	25.42
1775	10.60	8.44	8.76	7.48	54.84	179.11	173.48	0.70	24.89
2770	11.60	9.42	9.68	9.17	43.79	173.63	170.31	0.73	21.18
2892	11.92	9.77	9.66	9.55	41.06	172.13	168.51	0.76	20.16
3095	13.00	9.94	10.55	9.89	39.34	170.17	169.60	0.73	19.63
3209	12.91	10.04	10.18	9.91	38.33	169.21	168.99	0.76	19.21
4163	13.77	10.49	10.78	10.77	33.07	162.04	160.75	0.76	17.30
4196	13.91	10.67	10.63	11.37	31.86	159.76	158.58	0.76	16.76
4224	13.86	9.08	10.89	11.01	31.89	159.99	159.14	0.76	16.82

Claims:

1. A process for treating a mixed C4 stream comprising iso-butene and 1,3-butadiene, said process comprising:

a) reacting acetic acid with said stream in an addition reactor,

b) withdrawing from the addition reactor a product stream comprising iso-butene, sec-butenyl acetate, n-butenyl acetate and t-butyl acetate, and

c) recovering n-butenyl acetate from the product stream, characterised in that

d) t-butyl acetate is recycled to said addition reactor.

2. A process as claimed in Claim 1 wherein isobutene is recovered from the product stream.

3. A process as claimed in Claim 2 wherein the isobutene is recovered by distillation.

4. A process as claimed in any one of the preceding Claims wherein isobutene is recycled to the addition reactor.

5. A process as claimed in any one of the preceding Claims wherein the mixed C_4 stream is obtained by the dehydrogenation of butane or butene, or by the steam cracking of naphtha.

6. A process as claimed in any one of the preceding Claims wherein, in addition to the iso-butene and 1,3-butadiene, the mixed C_4 stream comprises one or more of isobutane, n-butane, 1-butene, trans-2-butene, cis-2-butene, 1,2-butadiene, propadiene, methyl acetylene, ethyl acetylene, dimethyl acetylene, vinyl acetylene, diacetylene, and C_5 acetylenes.

7. A process as claimed in any one of the preceding Claims wherein, in the addition reactor, the relative mole ratios of butadiene in the mixed C_4 stream to acetic acid is in

the range 1:1 to 1:10.

8. A process as claimed in any one of the preceding Claims wherein the addition reaction is carried out at a temperature in the range 40 to 90°C.

9. A process as claimed in any one of the preceding Claims wherein the addition reaction is carried out using a heterogeneous catalyst.

10. A process as claimed in Claim 9 wherein the heterogeneous catalyst comprises a zeolite or a strong acid ion-exchange resin.

11. A process as claimed in any one of the preceding Claims wherein water is present in the addition reaction in an amount between 0.5 and 20 w/w %, based on the total charge to the reactor.

12. A process as claimed in Claim 9 or 10 wherein the addition reaction is carried out under conditions of high shear.

13. A process as claimed in any one of the preceding Claims wherein a polymerisation inhibitor is added to the addition reaction mixture.

14. A process as claimed in any one of the preceding Claims wherein the n-butenyl acetate recovered from the product stream is hydrogenated to produce butyl acetate.

15. A process as claimed in any one of the preceding Claims wherein components of the product stream comprising t-butyl acetate, n-butenyl acetate and sec-butenyl acetate are separated from said product stream by azeotropic separative methods.

16. A process as claimed in any one of the preceding Claims wherein di-isobutene is recovered from the product stream.

INTERNATIONAL SEARCH REPORT

Inte nal Application No
PCT/GB 02/03930

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C07C67/04 C07C69/145

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, WPI Data, PAJ, CHEM ABS Data, BEILSTEIN Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DE 31 05 399 A (ERDOELCHEMIE GMBH) 21 October 1982 (1982-10-21) page 35 -page 37; example 12 ---	1-16
A	WO 00 26175 A (GRACEY BENJAMIN PATRICK ;KAMP NORBERT WALTER JOSEF (GB); BP CHEM I) 11 May 2000 (2000-05-11) cited in the application claims 1-8; examples 2,21-25 -----	1-16

[ ] Further documents are listed in the continuation of box C.

[X] 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

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
21 November 2002	02/12/2002

Name and mailing address of the ISA	Authorized officer
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	Kleidernigg, O

INTERNATIONAL SEARCH REPORT

Information on patent family members

Inte ɔnal Application No
PCT/GB 02/03930

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE 3105399 A	21-10-1982	DE 3105399 A1	21-10-1982
WO 0026175 A	11-05-2000	AU 6222199 A	22-05-2000
		CN 1332715 T	23-01-2002
		EP 1124784 A1	22-08-2001
		WO 0026175 A1	11-05-2000
		JP 2002528525 T	03-09-2002
		US 2002049351 A1	25-04-2002