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(54) **Title:** AN IMPROVED PROCESS FOR THE PREPARATION OF TERTIARY AMYL HYDROPEROXIDE

(57) **Abstract:** The present invention provides an improved process for the production of tertiary amyl hydroperoxide by the liquid phase oxidation of isopentane in presence of air or molecular oxygen as oxidant using the oxides of Group IIA metals such as magnesium, calcium, strontium and barium in high pressure reactor under stirring conditions at a temperature ranging between 110°-180°C and at moderate pressures for a period of 0.1- 12 h. The catalyst reused for several times without affecting its catalytic performance. The present invention produces a tertiary amyl hydroperoxide with 40-60 % selectivity and tertiary amyl alcohol, which has a numerius industrial applications.

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AN IMPROVED PROCESS FOR THE PREPARATION OF TERTIARY AMYL HYDROPEROXIDE

FIELD OF INVENTION

This invention relates to an improved process for the preparation of tertiary amyl hydroperoxide. More particularly the present invention relates to a process for the production t-amyl hydroperoxide by liquid phase oxidation of isopentane or a mixture of isopentane and n-pentane in presence of air or molecular oxygen as oxidant using alkaline earth oxide catalysts.

BACKGROUND OF THE INVENTION

Alkyl hydroperoxides are important intermediates and starting compounds for the production of valuable chemical derivatives. These can be used as a oxygen source instead of using pure oxygen. In the literature few processes have been reported for the preparation of alkyl hydroperoxides. The hydroperoxide can be prepared by reacting pure neutral dialkyl sulfate with alkali peroxide or with hydrogen peroxide in the presence of an alkali. Another method comprises reacting of monoalkyl sulfate with hydrogen peroxide followed by the neutralization of the non-aqueous portion of the reaction product and yields alkyl peroxide. Still another method comprises the production of hydroperoxides from the corresponding alcohols by treating the latter with hydrogen peroxide in the presence of certain dehydrating agents. The major drawback of these methods is the use of costly starting or intermediate material, e.g. hydrogen peroxide. Hence, one of the objectives of the present invention is to avoid the above defects and to provide an economic process for the preparation of alkyl hydroperoxide.

The interaction of alkanes – particularly branched alkanes with oxygen to produce alkyl hydroperoxides is essentially a non-catalytic reaction, but in the presence of catalysts higher yields are reported. The majority of literature available is on the formation of t-butyl hydroperoxide [TBHP] and cumene hydroperoxide [CHP]. Some literature on oxidation of isopentane to produce t-amyl hydroperoxide [TAHP] is also available.

US Patent 3,974,228 (1976) describes a process for the preparation of t-amyl hydroperoxide by the oxidation of isopentane in the presence of buffer comprising a basic or amphoteric compound of a metal selected from Group IIIB at 130° - 150°C and about 500-600 psig oxygen pressure. With the use of LaO, about 75% selectivity to TAHP is obtained but the conversions of isopentane are, however, poor.

US Patent 2,403,772 (1946) discloses a process for the production of tertiary butyl hydroperoxide (TBHP), which comprises reacting substantially equivolumetric vapors of isobutane and oxygen at superatmospheric pressure and at a temperature of about 160°C in presence of hydrogen bromide. The yield of TBHP obtained was 75 % based on oxygen consumption.

US Patent 2,845,461 describes a process for the production of TBHP by non-catalytic liquid phase isobutane oxidation with molecular oxygen at about 100° - 150°C and 500-700 psig pressures. Besides TBHP, tertiary butyl alcohol (TBA) is obtained as a other major side product, which has wide applications. Good isobutane conversions and a high yield to TBHP and TBA (> 90 %) have been reported.

US Patent 5,571,908 (1996) describes TBHP formation by isobutane oxidation using porphyrin complexes of Cu, Co, Zn, Mg, but the decomposition of the TBHP was also very rapid resulting in formation of t-butanol (~85%).

The production organic hydroperoxides by the oxidation of aryl alkyl hydrocarbons in the presence of various transition metal salt complexes has also been described in the literature. In US Patent 2,954,405, a process for the production of organic hydroperoxides by autooxidation of hydrocarbons in presence of molecular oxygen using metal phthalocynine as catalysts is disclosed. US Patent Nos. 5,025,101 and 5,183,945 describes a process for preparing organic hydroperoxides by selectively oxidizing aryl alkyl hydrocarbons to their corresponding organic hydroperoxides using tetranuclear manganese complexes as catalysts. US Patent 5,922,920 discloses the process for the production of organic hydroperoxide by oxidizing aryl alkyl hydrocarbons having a benzylic hydrogen with an oxygen containing gas using polynuclear transition metal aggregates. A process for the preparation of hydroperoxides in a homogeneous system by autooxidizing secondary alkyl group substituted methylbenzenes in the presence of water, a base and oxygen containing gas, and a water soluble chelate compound in which multidentate ligands are coordinated to at least one metal from the class of Co, Ni, Mn, Cu and Fe is disclosed in US Patent 4,013,725.

From the literature it can be seen that a very little work has been reported on the production of t-amyl hydroperoxide and hence there is a lot of scope for development of a process for the manufacture of TAHP. As seen from the above literature that most of the processes for the production of hydroperoxide are non-catalytic and it is advantageous to use the catalyst to

increase the yield of hydroperoxide. In the present invention a solid catalyst is used for the production of TAHP by the liquid phase oxidation of isopentane, which can be reused several times without losing the activity and selectivity.

The present invention provides a process for the preparation of alkyl hydroperoxide by the liquid phase oxidation of alkanes using alkaline earth oxides as a catalyst system in the presence of air or diluted oxygen as oxidant at moderate temperatures and pressures. This invention provides a process by the use of a heterogeneous catalyst system, which can be separated from the reaction mixture with ease and reused for the another recycle experiment without affecting the catalytic performance in oxidation of isopentane.

OBJECTIVES OF THE INVENTION

The main object of the present invention is to provide an improved process for the preparation of tertiary amyl hydroperoxide by the liquid phase oxidation of isopentane or a mixture of isopentane and n-pentane in the presence of air or molecular oxygen as oxidant using alkaline earth oxide catalysts.

Yet another object of the present invention is to provide a process for making tertiary amyl hydroperoxide with minimum by-products formation.

Yet another object of this invention is to provide catalytic liquid phase oxidation of isopentane process for the production of reaction products consisting predominantly tertiary amyl hydroperoxide and tertiary amyl alcohol.

Yet another object of this invention is to provide a process for the production of tertiary amyl hydroperoxide at moderate temperatures and pressures.

Yet another object of this invention is to use an isopentane and n-pentane mixture for the production of tertiary amyl hydroperoxide.

SUMMARY OF THE INVENTION

The present invention provides an improved process for the preparation of tertiary amyl hydroperoxide by the liquid phase oxidation of isopentane or a mixture of isopentane and n-pentane in presence of air or molecular oxygen as oxidant using a catalyst system consisting of oxides of alkaline earth metals. The reactions were carried out at a temperature ranging between 110°-180°C and at moderate pressure in the presence of air or molecular oxygen as an oxidant in a high-pressure Parr reactor for a period of 0.1- 12 h. After the reaction was completed, the reaction mixture was cooled to below 10°C, the reaction mixture was filtered and the reactants

and products were analyzed by gas chromatograph (GC). The products were also identified by gas chromatograph - mass spectroscopy (GCMS). The present invention produces alkyl hydroperoxide with good conversion (15-20 %) and selectivity (40-60 %) along with tertiary amyl alcohol and other byproducts such as alcohols and ketones.

DETAILED DESCRIPTION OF THE INVENTION

Accordingly, the present invention provides an improved process for the preparation of tertiary amyl hydroperoxide by the liquid phase oxidation of isopentane or a mixture of isopentane and n-pentane using a heterogeneous catalyst in the presence of air or molecular oxygen as an oxidant, and optionally in the presence of t-butyl hydroperoxide (TBHP) as initiator, at a temperature in the range of 110°-180°C, at a partial pressure of oxygen in the range of 10 – 1000 psig, for a period of 0.1- 12 hours, cooling the above said reaction mixture to 10°C, separating the catalyst to obtain the desired products by known method.

In an embodiment of the present invention the mole ratio of isopentane to n-pentane used in the mixture of isopentane and n-pentane is in the range of 90:10 and 10:90.

In yet another embodiment the heterogeneous catalysts used for this invention are the oxides and carbonates of Group IIA metals i.e. magnesium, calcium, strontium and barium.

In yet another embodiment the mole ratio of the isopentane to catalyst used is in the range of 0.5 to 200.

In yet another embodiment the mole ratio of isopentane to alkaline earth oxides or carbonates is in the range of 0.5 - 200.

In yet another embodiment the reaction temperature uesd is in the arnge of 120°- 150°C.

In yet another embodiment the time period used for the reaction is in the range of 2-10 hours.

In still another embodiment the catalyst used is recyclable for further reactions.

In still another embodiment the tertiary amyl alcohol is obtained as valuable by-product.

The novelty of the present invention lies in the use of alkaline earth oxide as reusable catalyst in the preparation of alkyl hydroperoxide by the liquid phase oxidation of alkanes of air or diluted oxygen as oxidant at moderate temperatures and pressures.

The following examples are given by the way of illustration and therefore should not be construed to limit the scope of the invention.

Example 1

A mixture of 37.0g isopentane, 0.8 g TBHP and 1.0 g MgO catalyst was charged to the stirred autoclave of 300 ml capacity having a temperature and pressure controller and water condenser. The reaction vessel was heated to 140°C and then pressurized the reactor up to 900 psig with air and continued the reaction for 2h. The reactor was refilled with oxygen by taking into account the absorbed oxygen in the reactor and the reaction further continued for 2h. At the end of the reaction, the reaction mixture was cooled to 10°C, filtered to separate the catalyst, and then weighed. The reactants and products were analyzed by gas chromatograph and the products were also identified by gas chromatography mass spectrometry. The GC analysis of reaction mixture showed 16.1 % conversion of isopentane with 52.4 % and 28.7 % selectivity to t-amyl hydroperoxide and t-amyl alcohol, respectively. Ethanol, acetone and acetic acid were formed as side products with 6.5%, 12.3% and 0.2 % selectivity, respectively.

Example 2

A mixture of 37.0g isopentane, 0.8 g TBHP and 1.0 g MgO catalyst was charged to the stirred autoclave of 300 ml capacity having a temperature and pressure controller and water condenser. The reaction vessel was heated to 140°C and then pressurized the reactor up to 900 psig with air and continued the reaction for 2h. At the end of the reaction, the reaction mixture was cooled to 10°C, filtered to separate the catalyst, and then weighed. The reactants and products were analyzed by gas chromatograph and the products were also identified by gas chromatography mass spectrometry. The GC analysis of reaction mixture showed 7.0 % conversion of isopentane with 61.3 % and 20.4 % selectivity to t-amyl hydroperoxide and t-amyl alcohol, respectively. Ethanol, acetone and acetic acid were formed as side products with 4.2%, 11.0% and 3.1 % selectivity, respectively.

Example 3

A mixture of 37.0g isopentane, 0.8 g TBHP and 1.0 g MgO catalyst was charged to the stirred autoclave of 300 ml capacity having a temperature and pressure controller and water condenser. The reaction vessel was heated to 140°C and then pressurized the reactor up to 900 psig with air and continued the reaction for 2h. The reactor was refilled with oxygen by taking into account

the absorbed oxygen in the reactor and the reaction further continued for 6h. At the end of the reaction, the reaction mixture was cooled to 10°C, filtered to separate the catalyst, and then weighed. The reactants and products were analyzed by gas chromatograph and the products were also identified by gas chromatography mass spectrometry. The GC analysis of reaction mixture showed 21.9 % conversion of isopentane with 45.0 % and 34.0 % selectivity to t-amyl hydroperoxide and t-amyl alcohol, respectively. Ethanol, acetone and acetic acid were formed as side products with 6.5%, 12.9% and 1.7% selectivity, respectively.

Example 4

A mixture of 37.0 g isopentane, 0.8 g TBHP and 0.5 g MgO catalyst was charged to the stirred autoclave of 300 ml capacity having a temperature and pressure controller and water condenser. The reaction vessel was heated to 140°C and then pressurized the reactor up to 900 psig with air and continued the reaction for 2h. The reactor was refilled with oxygen by taking into account the absorbed oxygen in the reactor and the reaction further continued for 2h. At the end of the reaction, the reaction mixture was cooled to 10°C, filtered to separate the catalyst, and then weighed. The reactants and products were analyzed by gas chromatograph and the products were also identified by gas chromatography mass spectrometry. The GC analysis of reaction mixture showed 19.9 % conversion of isopentane with 17.8 % and 44.0 % selectivity to t-amyl hydroperoxide and t-amyl alcohol, respectively. Ethanol, acetone and acetic acid were formed as side products with 12.5%, 21.9% and 3.8 % selectivity, respectively.

Example 5

A mixture of 37.0 g isopentane, 0.8 g TBHP and 2.0 g MgO catalyst was charged to the stirred autoclave of 300 ml capacity having a temperature and pressure controller and water condenser. The reaction vessel was heated to 140°C and then pressurized the reactor up to 900 psig with air and continued the reaction for 2h. The reactor was refilled with oxygen by taking into account the absorbed oxygen in the reactor and the reaction further continued for 2h. At the end of the reaction, the reaction mixture was cooled to 10°C, filtered to separate the catalyst, and then weighed. The reactants and products were analyzed by gas chromatograph and the products were also identified by gas chromatography mass spectrometry. The GC analysis of reaction mixture showed 18.3 % conversion of isopentane with 39.5 % and 34.8 % selectivity to t-amyl hydroperoxide and t-amyl alcohol, respectively. Ethanol, acetone and acetic acid were formed as side products with 8.7%, 15.8% and 1.2 % selectivity, respectively.

Example 6

A mixture of 37.0 g isopentane, 0.8 g TBHP and 1.0 g MgO catalyst was charged to the stirred autoclave of 300 ml capacity having a temperature and pressure controller and water condenser. The reaction vessel was heated to 120°C and then pressurized the reactor up to 900 psig with air and continued the reaction for 2h. The reactor was refilled with oxygen by taking into account the absorbed oxygen in the reactor and the reaction further continued for 2h. At the end of the reaction, the reaction mixture was cooled to 10°C, filtered to separate the catalyst, and then weighed. The reactants and products were analyzed by gas chromatograph and the products were also identified by gas chromatography mass spectrometry. The GC analysis of reaction mixture showed 3.3 % conversion of isopentane with 74.9 % and 12.5 % selectivity to t-amyl hydroperoxide and t-amyl alcohol, respectively. Ethanol, acetone and acetic acid were formed as side products with 2.9%, 5.7% and 4.1 % selectivity, respectively.

Example 7

A mixture of 37.0 g isopentane, 0.8 g TBHP and 1.0 g CaO catalyst was charged to the stirred autoclave of 300 ml capacity having a temperature and pressure controller and water condenser. The reaction vessel was heated to 140°C and then pressurized the reactor up to 900 psig with air and continued the reaction for 2h. The reactor was refilled with oxygen by taking into account the absorbed oxygen in the reactor and the reaction further continued for 2h. At the end of the reaction, the reaction mixture was cooled to 10°C, filtered to separate the catalyst, and then weighed. The reactants and products were analyzed by gas chromatograph and the products were also identified by gas chromatography mass spectrometry. The GC analysis of reaction mixture showed 15.3% conversion of isopentane with 20.5 % and 45.7 % selectivity to t-amyl hydroperoxide and t-amyl alcohol, respectively. Ethanol, acetone and acetic acid were formed as side products with 12.3%, 21.2% and 0.3 % selectivity, respectively.

Example 8

A mixture of 37.0 g isopentane, 0.8 g TBHP and 1.0 g CaO catalyst was charged to the stirred autoclave of 300 ml capacity having a temperature and pressure controller and water condenser. The reaction vessel was heated to 120°C and then pressurized the reactor up to 900 psig with air and continued the reaction for 2h. The reactor was refilled with oxygen by taking into account the absorbed oxygen in the reactor and the reaction further continued for 2h. At the end of the reaction, the reaction mixture was cooled to 10°C, filtered to separate the catalyst, and then

weighed. The reactants and products were analyzed by gas chromatograph and the products were also identified by gas chromatography mass spectrometry. The GC analysis of reaction mixture showed 3.5% conversion of isopentane with 76.1 % and 11.4 % selectivity to t-amyl hydroperoxide and t-amyl alcohol, respectively. Ethanol, acetone and acetic acid were formed as side products with 1.7 %, 6.0 % and 4.8 % selectivity, respectively.

Example 9

A mixture of 37.0 g isopentane, 0.8 g TBHP and 1.0 g BaO catalyst was charged to the stirred autoclave of 300 ml capacity having a temperature and pressure controller and water condenser. The reaction vessel was heated to 140°C and then pressurized the reactor up to 900 psig with air and continued the reaction for 2h. The reactor was refilled with oxygen by taking into account the absorbed oxygen in the reactor and the reaction further continued for 2h. At the end of the reaction, the reaction mixture was cooled to 10°C, filtered to separate the catalyst, and then weighed. The reactants and products were analyzed by gas chromatograph and the products were also identified by gas chromatography mass spectrometry. The GC analysis of reaction mixture showed 22.6 % conversion of isopentane with 14.8 % and 54.0 % selectivity to t-amyl hydroperoxide and t-amyl alcohol, respectively. Ethanol, acetone and acetic acid were formed as side products with 12.8%, 17.7% and 0.6 % selectivity, respectively.

Example 10

A mixture of 37.0 g isopentane, 0.8 g TBHP and 1.0 g $MgCO_3$ catalyst was charged to the stirred autoclave of 300 ml capacity having a temperature and pressure controller and water condenser. The reaction vessel was heated to 140°C and then pressurized the reactor up to 900 psig with air and continued the reaction for 2h. The reactor was refilled with oxygen by taking into account the absorbed oxygen in the reactor and the reaction further continued for 2h. At the end of the reaction, the reaction mixture was cooled to 10°C, filtered to separate the catalyst, and then weighed. The reactants and products were analyzed by gas chromatograph and the products were also identified by gas chromatography mass spectrometry. The GC analysis of reaction mixture showed 15.2 % conversion of isopentane with 12.5 % and 44.5 % selectivity to t-amyl hydroperoxide and t-amyl alcohol, respectively. Ethanol, acetone and acetic acid were formed as side products with 13.8%, 28.2% and 2.8 % selectivity, respectively.

Example 11

A mixture of 37.0 g isopentane and 1.0 g MgO catalyst was charged to the stirred autoclave of 300 ml capacity having a temperature and pressure controller and water condenser. The reaction vessel was heated to 140°C and then pressurized the reactor up to 900 psig with air and continued the reaction for 2h. The reactor was refilled with oxygen by taking into account the absorbed oxygen in the reactor and the reaction further continued for 2h. At the end of the reaction, the reaction mixture was cooled to 10°C, filtered to separate the catalyst, and then weighed. The reactants and products were analyzed by gas chromatograph and the products were also identified by gas chromatography mass spectrometry. The GC analysis of reaction mixture showed 9.2 % conversion of isopentane with 60.2 % and 19.9 % selectivity to t-amyl hydroperoxide and t-amyl alcohol, respectively. Ethanol, acetone and acetic acid were formed as side products with 5.8%, 9.4% and 3.6 % selectivity, respectively.

Example 12

A mixture of 18.0 g isopentane, 18.0g n-pentane, 0.8 g TBHP and 1.0 g MgO catalyst was charged to the stirred autoclave of 300 ml capacity having a temperature and pressure controller and water condenser. The reaction vessel was heated to 140°C and then pressurized the reactor up to 900 psig with air and continued the reaction for 2h. The reactor was refilled with oxygen by taking into account the absorbed oxygen in the reactor and the reaction further continued for 2h. At the end of the reaction, the reaction mixture was cooled to 10°C, filtered to separate the catalyst, and then weighed. The reactants and products were analyzed by gas chromatograph and the products were also identified by gas chromatography mass spectrometry. The GC analysis of reaction mixture showed 16.7 % conversion of isopentane and about 4.0 % conversion of n-pentane, with 45.5 % and 15.8 % selectivity to t-amyl hydroperoxide and t-amyl alcohol, respectively. Ethanol, acetone and acetic acid were formed as side products with 6.0%, 11.6% and 0.5 % selectivity, respectively and 20.7 % selectivity to 2-pentanol.

Catalyst recycle

Example 13

A mixture of 37.0 g isopentane, 0.8 g TBHP and 1.0 g MgO (recovered by the filtration of the reaction mixture followed by drying and calcination at 700°C for 6 h) catalyst was charged to the stirred autoclave of 300 ml capacity having a temperature and pressure controller and water condenser. The reaction vessel was heated to 140°C and then pressurized the reactor up to 900

psig with air and continued the reaction for 2h. The reactor was refilled with oxygen by taking into account the absorbed oxygen in the reactor and the reaction further continued for 2h. At the end of the reaction, the reaction mixture was cooled to 10°C, filtered to separate the catalyst, and then weighed. The reactants and products were analyzed by gas chromatograph and the products were also identified by gas chromatography mass spectrometry. The GC analysis of reaction mixture showed 16.7 % conversion of isopentane with 57.2 % and 25.8 % selectivity to t-amyl hydroperoxide and t-amyl alcohol, respectively. Ethanol, acetone and acetic acid were formed as side products with 6.6%, 10.2% and 0.3 % selectivity, respectively.

The advantages of the present invention are

1. The present invention provides an improved process for the production of tertiary amyl hydroperoxide by direct catalytic liquid phase oxidation of isopentane or a mixture of isopentane and n-pentane in presence of air or molecular oxygen as oxidant at ambient temperature and moderate pressure conditions.
2. The present invention provides a process by the use of heterogeneous catalysts system, which can be separated from the reaction mixture and reused for the reaction.
3. The present invention produces predominantly tertiary amyl hydroperoxide with 40-60 % selectivity and also tertiary amyl alcohol, which has a numerous industrial applications.
4. The catalyst system reported in the present invention is very cheap and hence the process is more economic.

We Claim:

1. An improved process for the production of tertiary amyl hydroperoxide by the liquid phase oxidation of isopentane or a mixture of isopentane and n-pentane using a heterogeneous catalyst in the presence of air or molecular oxygen as an oxidant, and optionally in the presence of t-butyl hydroperoxide (TBHP) as initiator and air or molecular at a temperature in the range of 110°-180°C ,at a partial pressure of oxygen in the range of 10 – 1000 psig, for a period of 0.1- 12 h, cooling the above said reaction mixture to 10°C, separating the catalyst and the desired product by known method.
2. A process as claimed in claim 1, wherein the mole ratio of isopentane to n-penatne used in the mixture of isopentane and n-pentane is in the range of 90:10 and 10:90.
3. A process as claimed in claim 1, wherein the heterogeneous catalyst used is selected from oxides carbonates of Group IIA metals selected from the group consisting of magnesium, calcium, strontium and barium.
4. A process as claimed in claim 1, wherein the mole ratio of the isopentane to catalyst used is in the range of 0.5 to 200.
5. A process as claimed in claim 1, wherein the reaction temperature used is in the of 120°-150°C.
6. A process as claimed in claim 1, wherein the time period used for the reaction is in the arnge of 2-10 hours.
7. A process as claimed in claim 1, wherein the heterogeneous catalyst used is recyclable for further reactions.
8. A process as claimed in claim 1, wherein the tertiary amyl alcohol is obtained as valuable by-product.

INTERNATIONAL SEARCH REPORT

International application No
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A. CLASSIFICATION OF SUBJECT MATTER
INV. C07C409/04

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 practical, search terms used)
EPO-Internal, CHEM ABS Data, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 152 358 A (BARONE, BRUNO J.) 1 May 1979 (1979-05-01) column 1, lines 52-57; column 3, lines 36-37; column 3, lines 42-44; column 3, line 67 - column 4, line 3; column 4, lines 7-9; column 4, lines 27-37; Tables I and II; claims	1-8
X	US 3 974 228 A (BARONE ET AL) 10 August 1976 (1976-08-10) cited in the application column 5, Table II; claims	1-8
X	US 2 447 794 A (BREWER PHILIP D) 24 August 1948 (1948-08-24) column 3, lines 40-45; column 3, lines 56-67; column 4, lines 52-54; claims	1-8

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
20 April 2006	24/05/2006

Name and mailing address of the ISA/	Authorized officer
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4152358 A	01-05-1979	NONE	
US 3974228 A	10-08-1976	NONE	
US 2447794 A	24-08-1948	NONE	