

Clarke, Modet & C°
COLOMBIA

ESCOBAR - URIBE ASOCIADOS
Intellectual Property

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As. 2853/PCT.

**SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO
DIVISIÓN DE NUEVAS CREACIONES**

E. S. D.

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO



No. 05-067804- -00004-0000

Ref.: Expediente No. **05-067.804**
Solicitud de Patente a nombre de
DSM IP Assets B.V.

RECIBO 2007-09-20 15:51:37 Dep. 2020 NUECREACIONE
C.C. 11 PATENTEYII Eve: 379 FASENACIONALII
Act. 516 PETICION Folios: 3

Yo, **JIMENA ESCOBAR URIBE**, identificada como aparece al pie de mi firma, domiciliada en Bogotá, en la Carrera 11 No. 86-53, piso 6, obrando como apoderada de la sociedad **DSM IP Assets B.V.**, con domicilio en Heerlen, Holanda, solicitante de la patente de la referencia, pido a usted que se proceda a examinar si la invención, cuya patente se tramita en el expediente de la referencia, es patentable.

Adjunto al presente memorial los recibos No. 07 - 75,110 de 17 de septiembre de 2007 y 07 - 67,844 de 22 de agosto de 2007, por la suma de \$202.000.00, con lo cual queda cubierta la tasa oficial correspondiente a dicho estudio.

Señor Superintendente,


JIMENA ESCOBAR URIBE
C.C.39.779.452 de Usaquén
T.P. 68.228

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SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO



N

Fecha: 20

Trá: 1: F

Act: 53: F

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO

NIT : 800176089-2

RECIBO OFICIAL DE CAJA : 07 - 75,110
FECHA : SEPTIEMBRE 17 DE 2007

***** CONSIGNACION *****

DEPOSITANTE	TIPO PAGO	BANCO	CUENTA	No. PAGO	FECHA PGO	Vr. PAGO
CLARKE MODET Y CO. COLOMB	CONSIGNACION	BANCO POPULAR	050-00110-6	67354914	17/09/2007	2,254,000.00

***** CONCEPTO *****

CANT.	RENTISTICO	CONCEPTO	TOTAL CONCEPTO
1	50005-01-01	SOLICITUDES	115 PTC CAP-II EXAMEN DE PATENTIBILIDAD
			TOTAL : 135,000.00

SON: CIENTO TREINTA Y CINCO MIL PESOS

RESPONSABLE : _____

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SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO

RECEPCION DE PAGOS

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SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO

NIT : 900176009-2

RECIBO OFICIAL DE CAJA : 07 - 67,844
FECHA : AGOSTO 22 DE 2007

***** CONSIGNACION *****

DEPOSITANTE	TIPO PAGO	BANCO	CUENTA	Nº. PAGO	FECHA PGO	VR. PAGO
CLARKE MODET Y CO. COLOMBIA	CONSIGNACION	BANCO POPULAR	050-00110-6	67350168	22/08/2007	8,776,000.00

***** C O N C E P T O *****

CANT.	RENTISTICO	CONCEPTO	VR. CONCEPTO
1	50005-01-01	SOLICITUDES	
		03 INVOCACION DE UNA PRIORIDAD EN S	68,000.00
		TOTAL :	68,000.00

SON: SESENTA Y OCHO MIL PESOS

RESPONSABLE : _____

RECIBO DE CAJA APLICADO AL EXPEDIENTE No. _____

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DIVISION DE NUEVAS CREACIONES

RADICACIÓN EXPEDIENTE No 05-67804

EL EXTRACTO DE LA PRESENTE SOLICITUD DE **PATENTE DE INVENCION**

FUE PUBLICADO EN LA GACETA DE PROPIEDAD INDUSTRIAL No **575** DE

FECHA **30 DE ABRIL DE 2007** EL TERMINO HABIL SEÑALADO POR LA LEY

EXPIRA EL **31 DE JULIO DEL 2007**

NOTA: Dentro del plazo de los seis (6) meses siguientes a partir de la fecha de publicación en la gaceta de Propiedad Industrial, deberá solicitar y cancelar el examen de patentabilidad so pena de que la solicitud caiga en abandono, de acuerdo con lo establecido en el Artículo 44 de la Decisión 486/2000.

SE PRESENTARON OPOSICIONES POR PARTE DE TERCEROS.

SI _____

NO ___X___

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SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO
DIVISION DE NUEVAS CREACIONES

Bogotá, D.C., 23 de septiembre de 2008

Apoderado: Jimena Escobar Uribe

ASUNTO	Radicación	05-67804
	Trámite	002
	Evento	001
	Actuación	430
	Oficio	13290
	Folios	014

Como resultado del examen de fondo, realizado con fundamento en el artículo 45 de la Decisión 486 de la Comisión de la Comunidad Andina, se le comunica:

1. Documentos estudiados

- 1.1. Descripción: Folios: 09 a 26 como se radicó inicialmente.
- 1.2. Reivindicaciones: Folios: 27 a 31 como se radicó inicialmente
- 1.3. Prioridad: Folio 1: 60/436.476; 27/dic/2002

2. Objeto de la invención

Título de la solicitud: "PROCESO PARA REDUCIR LA CONCENTRACIÓN DE ALDEHIDO EN UNA MEZCLA QUE COMPRENDE CICLOHEXANONA Y UNO O MÁS ALDEHIDOS"

El objeto de la presente solicitud de patente de invención consiste en:
Un proceso para reducir la concentración de aldehído en una mezcla que comprende ciclohexanona y uno o más aldehídos, dicho proceso comprende la destilación de dicha mezcla en una columna de destilación en presencia de un compuesto alcalino, en donde en el fondo de la columna de destilación sustancialmente no está presente el agua.
Reivindicaciones 1-17: Proceso para reducir la concentración de aldehído en una mezcla.

El objeto de la invención definido anteriormente se clasifico de acuerdo con la Clasificación Internacional de Patentes (IPC) : C07C 45/85, A61K31/12, A61K31/11.

3. De la solicitud de Patente

3.1. Reivindicaciones (artículo 30 D 486)

Para la reivindicación 1 se encuentra el término relativo “sustancialmente”. Se requiere hacer la corrección respectiva.

4. Determinación del Estado de la Técnica

Considerando que la fecha de presentación de la primera solicitud de patente de la cual se reivindica prioridad es 27 de Diciembre de 2002, se consultaron las bases de datos y los archivos con que cuenta la entidad con fecha de publicación anterior y se encontraron los siguientes documentos que anticipan el objeto de esta solicitud:

Nº	Documento	Título	Fecha de Publicación*
D1	GB 2028329	Purification of the cycloalkanones obtained by oxidation of cycloalkanes	05/mar/1980
D2	GB 1276792	Acetone purification process	07/jun/1972

6. Análisis de patentabilidad (artículo 14 D486)

6.1. Novedad (artículo 16 D486)

Comparando elemento por elemento el objeto de esta solicitud con lo mencionado en las anterioridades, tenemos que:

La solicitud en estudio reclama un proceso para reducir la concentración de aldehído en una mezcla que comprende ciclohexanona y uno o más aldehídos, dicho proceso comprende la destilación de dicha mezcla en una columna de destilación en presencia de un compuesto alcalino, en donde en el fondo de la columna de destilación sustancialmente no está presente el agua.

-D1 [GB 2028329] enseña un proceso para la purificación o separación de ciclohexanona de los indeseados aldehídos, de una mezcla que contiene una cicloalcanona de C5-C12 en el anillo, y los respectivos aldehídos, obtenida por la

oxidación del correspondiente cicloalcano en fase líquida. A esta mezcla se le agrega a destilar se le agrega una solución de hidróxido de sodio o un carbonato de metal alcalino, en una cantidad que depende de la concentración del aldehído, de la base usada y la temperatura de destilación. Usualmente la concentración de la base libre en la solución acuosa es de 0.1 mol/L. Entonces puede llegar a considerarse que es sustancialmente libre de agua la destilación, dependiendo de la cantidad de mezcla a separar y de la concentración de aldehído contenida en la mezcla. Porque el volumen de la mezcla cicloalcanona/aldehídos puede ser de varios litros y el catalizador alcalino (hidróxido de metal alcalino o carbonato) en cantidad de uno o dos mililitros, entonces el proceso es “sustancialmente libre de agua”, porque solamente contendría ppm de agua, indicándose que es menos de 100 ppm en peso de agua que está presente en la columna de destilación y es el mismo proceso que la presente solicitud reclama como nuevo e inventivo, por lo tanto carece de novedad.

-Cuando una invención está afectada por novedad obviamente no posee nivel inventivo.

4.1. **Nivel inventivo** (Artículo 18 D486 de la C.A.N)

D2 [GB 1276792] describe un proceso para la separación de la preparación de acetona de impurezas, que son los aldehídos, convirtiendo tales aldehídos en polímeros no volátiles. El proceso de purificación se lleva a cabo en una columna de destilación de multiplatos, y puede usarse como catalizador un catalizador alcalino en solución, luego el agua es removida constantemente de la columna de destilación, cuando se agrega pequeñas cantidades en solución, o también se puede agregar exento de agua, en forma de óxidos alcalinos. Si se compara el proceso enseñado por D2 y el proceso de la presente solicitud observamos que la única diferencia es que no aparece el nombre explícito de la ciclohexanona, porque como proceso de purificación de cetonas es exactamente el mismo proceso de separación una mezcla de cetona/ aldehído, por lo tanto para una persona normalmente versada puede probar con una alta probabilidad de éxito el proceso en cualquier mezcla que contenga cetonas a purificar de impurezas llamadas aldehídos. De tal manera que esta oficina no observa el aporte real al acervo tecnológico, y por lo tanto no se puede considerar que tenga nivel inventivo.

5. **Conclusión:**

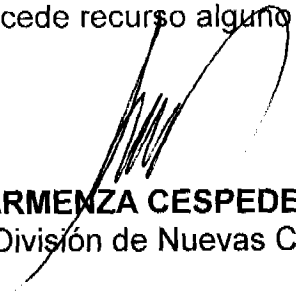
Los requisitos de patentabilidad de la presente solicitud se encuentran afectados así:

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N° Documento	Reivindicaciones Afectadas	Requisito que Afecta
D1	1 a 17	No vedad y Nivel Inventivo
D2	1 a 17	Nivel Inventivo

En cumplimiento del artículo 45 de la Decisión 486 de la Comisión de la Comunidad Andina, se le indica que debe dar respuesta dentro del término de sesenta días contados a partir de la fecha de notificación de la presente comunicación. En caso de no dar respuesta al presente requerimiento, o si a pesar de la respuesta subsistieran los impedimentos para la concesión, se denegará la patente.

Notifíquese el presente oficio conforme a lo dispuesto en el artículo 8 de la resolución reglamentaria No. 00210 del 15 de enero de 2001, advirtiéndole que contra él no procede recurso alguno en la vía gubernativa.


ALIX CARMENZA CESPEDES DE VERGEL
Jefe de División de Nuevas Creaciones

El anterior requerimiento fue notificado por fijación en lista, de fecha
17 OCT 2000

CONCEPTO TECNICO No. 3015	EXAMINADOR TECNICO Cód. No. 202012
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19/10/79-120
P2 (6115-1.3)

(12) UK Patent Application (19) GB (11) 2 028 329 A

- (21) Application No 7928080
(22) Date of filing 13 Aug 1979
(23) Claims filed 13 Aug 1979
(30) Priority data
(31) 7808416
(32) 12 Aug 1978
(33) Netherlands (NL)
(43) Application published 5 Mar 1980
(51) INT CL³
C07C 45/78 45/33 48/385
(52) Domestic classification
C2C 1175 1177 221 225
227 22Y 297 30Y 351 353
386 409 40Y 413 416 43X
625 GX UE
(56) Documents cited
GB 1420511
GB 1104160
GB 1060484
GB 1018557
(58) Field of search
C2C
(71) Applicants
Stamicarbon B.V., P.O.
Box 10, Geleen, the
Netherlands
(72) Inventor
Otto Gerrit Plantema
(74) Agents
Hyde, Heide & O'Donnell

(54) Purification of cycloalkanones obtained by oxidation of cycloalkanes

(57) The purification of a C₅-C₁₂ cycloalkanone e.g. cycloalkane, obtained by oxidation of the corresponding cycloalkane, is effected by subjecting the cycloalkanone to an aldol condensation whereby at least 80% of the aldehydes present are converted but not more than 20% of cycloalkyl esters derived from carboxylic acids containing at least 4 carbon atoms per molecule, is allowed to saponify. In effecting the aldol condensation an alkaline catalyst may be used, e.g. sodium hydroxide or sodium carbonate, or an acid catalyst may be used e.g. sulphuric acid or an acid in exchanger. After the aldol condensation has been effected the cycloalkanone may be separated by distillation.

GB 2 028 329 A

SPECIFICATION

Process for the purification of cycloalkanone mixtures obtained in the oxidation of cycloalkanes

The invention relates to a process for the purification of mixtures that contain a cycloalkanone containing 5-12 carbon atoms in the ring and which have been obtained by the oxidation of the corresponding cycloalkane in the liquid phase by means of a gas containing molecular oxygen.

The preparation of cycloalkanone mixtures by oxidation of the corresponding cycloalkane in the liquid phase by means of a gas containing molecular oxygen is well known (see, e.g., the general surveys in the Stanford Research Institute Reports 3 (1965), 3A (1971), 7 (1965), 307-319, and 7A (1968), 87-103). In most cases use is made of a degree of conversion of 1-12% calculated to the cycloalkane feed stock, so that the resulting reaction mixture contains a large proportion of unconverted cycloalkane. The mixture furthermore contains, in addition to the cycloalkanone a considerable amount of the corresponding cycloalkanol in most instances, and a minor proportion of secondary products, including aldehydes, organic acids and cycloalkyl esters. It is common practice to process the reaction mixture by distillation, when the cycloalkane and the by-products that are more volatile than the cycloalkane, and including a large part of the aldehydes, are distilled off first, followed by the cycloalkanone and finally the cycloalkanol. The residue consists of high-boiling cycloalkyl esters and other products.

According to a known process procedure the yield of cycloalkanol is improved by saponifying the cycloalkyl esters present in the reaction mixture after distillation of the cycloalkane by treatment with an aqueous solution of sodium hydroxide or sodium carbonate. This process has the disadvantage, that the stringent conditions required for the saponification of the high-boiling cycloalkyl esters, which are difficult to saponify, cause the cycloalkanol to be converted by self-condensation into the corresponding 2-cycloalkylidene cycloalkanone, thus becomes lost (Netherlands published Patent Application 6600638). The remedy for this problem is to wash the reaction mixture with dilute aqueous solutions of alkali hydroxides or alkali carbonates under such mild conditions that only the organic acids dissolved in the organic phase are neutralized and no saponification of cycloalkyl esters is effected. The product thus obtained is distilled and then saponified with an aqueous alkali solution. By this means of loss of cycloalkanone by self-condensation is avoided.

It however has been found that a cycloalkanone prepared in this way, particularly cyclohexanone, does not meet the demands normally required for its use. Thus when the cyclohexanone is processed into polycaprolactam (nylon-6) by oxidation, Beckmann rearrangement and polymerization, the mechanical strength of the polycaprolactam obtained leaves much to be desired. It is now considered that this is due to the fact that a small part of the aldehydes persistently combines with the cyclohexanone fraction. When the cyclohexanone is processed into

polycaprolactam, the aldehydes, even if present in low concentrations, give rise to impurities with a highly deleterious effect on the strength of the polycaprolactam. Other cycloalkanones with 6-12 carbon atoms in the ring show a similar effect.

The invention is directed to a process for the purification of cycloalkanone mixtures without any appreciable loss of cycloalkanone by self-condensation, and is based on the discovery that condensation of aldehydes with themselves or with cycloalkanone, can be effected at reaction conditions milder than those at which substantial self-condensation of cycloalkanone occurs.

The invention provides a process for the purification of a mixture containing a cycloalkanone containing 5-12 carbon atoms in the ring obtained by the oxidation of the corresponding cycloalkane in the liquid phase by means of a gas containing molecular oxygen, characterized in that the said mixture containing the cycloalkanone is subjected to an aldol condensation reaction by which at least 80% of the aldehydes present are converted, but not more than 20% of cycloalkyl esters derived from carboxylic acids containing at least 4 carbon atoms per molecule is allowed to saponify.

The strong acid or free base which is present in the aldol condensation is necessary as otherwise the aldehydes will not condense with themselves or with the cycloalkanone to form the higher-boiling products. It is in this respect that the process according to the invention differs from the process according to Netherlands Patent Application 6600638. Preferably the aldol condensation is performed with a basic catalyst usually in the form of an aqueous solution. Usually a minimum concentration of free base in the aqueous solution of 0.1 mole/l is used, but the actual minimum requirement depends on the reaction temperature, the particular basic catalyst, the aldehyde concentration, and the amount of aqueous solution used. The reaction conditions such as temperature, nature of the basic catalyst, amount of free base, amount of aqueous solution, duration of treatment and the like, are selected so that not more than a minor proportion of the cycloalkyl esters that are difficult to saponify are saponified. This requirement ensures the avoidance of any appreciable loss of cycloalkanone by self-condensation. A person skilled in the art can determine suitable combinations of reaction conditions from some very simple experiments.

In the aldol condensation it is preferred to convert not more than 0.2% cycloalkanone in excess of that required for the removal of the aldehydes. It is possible in practice to restrict the loss of cycloalkanone by self-condensation to less than 0.02%.

The reaction temperature preferably is in the range between 30 and 100°C, particularly between 60 and 95°C. The pressure may be, for instance in the range between 10 and 1000 kPa, preferably between 50 and 200 kPa.

Particularly suitable solutions of those which may be used in the aldol condensation are aqueous solutions of alkali-metal hydroxides and carbonates, preferably sodium hydroxide or sodium carbonate. Particularly useful solutions are those containing from

DI

100% mol.

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0.5 to 15, more in particular 1 to 5, wt. % aqueous sodium hydroxide solution. The amount of aqueous base solution added is preferably 1 to 20 wt. % with respect to the organic phase. A strongly basic ion exchanger can also be used advantageously as the basic catalyst.

The duration of treatment may, for instance be in the range between 5 and 60 minutes, preferably between 30 and 60 minutes, at an alkali concentration of about 4% by weight, or between 5 and 15 minutes at an alkali concentration of about 15% by weight.

Analogous considerations apply when use is made of aldol condensation catalysed by a strong acid. Suitable strong acids are for example those containing from 0.1 to 20% by weight aqueous sulphuric acid or a corresponding concentration of p-toluene sulphonic acid, or preferably strongly acid ion exchangers containing sulphonic acid groups. At too high acid concentrations there is the risk of undesirable secondary reactions. The amount of strong acid may be a catalytic amount and range, for instance between 0.01 and 10% by weight based on the organic phase, preferably between 0.05 and 0.5% by weight. An advantage of the acid-catalysed reaction is that a lower reaction temperature of, e.g., 30-60°C and/or a shorter reaction period suffice. Use may also be made of temperatures up to 100°C.

The mixtures to be treated usually contain 50 to 1000 parts by weight per million of aldehydes.

The aldol condensation reaction can be effected in a stirred reactor, but use is preferably made of a plug-flow reactor.

By preference such reaction conditions are used that not more than 10% of better still not more than 5% of the cycloalkyl esters derived from carboxylic esters with at least 4 carbon atoms per molecule, is saponified.

The aldol condensation reaction is preferably effected after part or, preferably substantially all of the unconverted cycloalkane has been removed from the reaction mixture of the oxidation reaction. In order to remove organic acids, the mixture may have been subjected to a treatment with water or to a neutralization treatment as described above. If so desired part of the aldehydes, together with other by-products with a lower boiling point than the cycloalkanone, may be distilled off before the aldol condensation.

The product mixture of the aldol condensation may be freed of the acidic or basic catalyst, e.g., by washing with water or by neutralization. If an ion exchanger is used as the catalyst, washing or neutralization may be omitted. The cycloalkanone is preferably then separated e.g. by distillation, from the resulting aldol-condensation products, especially if the cycloalkanone is to be processed into a polyacetam. However this is not necessary for some end-uses for cycloalkanones. Cycloalkanol that is also recovered can be dehydrogenated into a further amount of cycloalkanone in known manner. The distillation residue contains cycloalkyl esters, which can be hydrolyzed in known manner to obtain another amount of cycloalkanol.

Aldol condensation of aldehydes with cycloal-

kanones is known, e.g. from German Auslegeschrift 1,085,520 and J. Am. Chem. Soc. 29 (1964), 1347.

These publications however deal with the reaction of the two reagents in a pure form and in molar ratios of between 1:1 and 1:10. It cannot be inferred from such disclosures that very small proportions of aldehydes could be removed from the much greater amounts of cycloalkane-oxidation products containing cycloalkanone in the way according to the invention.

A further explanation is given in the schematic reaction diagram of the accompanying drawing. The diagram relates to cycloalkanone cyclohexanone, but the process of the invention is also suitable for the purification of other cycloalkanones with 5-12 carbon atoms in the ring, e.g. cyclopentanone or cyclododecanone.

Cyclohexane is passed through line 1 to reactor 2. Air or another gas containing molecular oxygen is fed through line 3 to reactor 2 in which a liquid phase of cyclohexane and oxidation products is maintained. Vent gas escapes through line 4. Cyclohexane vapour contained therein is condensed in a device (not shown) and is returned to reactor 2. The liquid reaction mixture flows through line 5 to neutralization device 6, e.g. a mixer-settler, in which it is washed with an aqueous sodium-carbonate solution supplied through line 7. The amount of sodium carbonate is such that no unconverted base remains in neutralizing device 6. The aqueous phase is discharged through line 8 and a vapour phase through line 9. Cyclohexane is condensed from the vapour phase and returned to reactor 2. The organic liquid phase flows through line 10 to distillation column 11, where the unconverted cyclohexane is removed. The vapour is discharged through line 12, condensed and returned to reactor 2. The distillation residue, which substantially consists of cyclohexanone and cyclohexanol and also contains esters and

aldehydes, passes through line 13 to aldol-condensation vessel 14, to which an aqueous sodium hydroxide solution is fed through line 15. The reaction mixture of the aldol condensation flows through line 16 to washing column 17 where it is washed in counter-current relation to water supplied through line 18 to remove traces of hydroxide. If so desired, cyclohexane may be fed to washing device 17 through lines 18 and 16 to improve phase separation. The washing device may be a mixer-settler instead of a column. The washing water, together with the aqueous phase of the reaction product of the aldol condensation, leaves washing device 17 through line 20, while the washed organic mixture is fed through line 21 to distillation column 22, where a fraction (i.e. pentanol and heptanone) with a lower boiling point than cyclohexanone, is distilled off. The light fraction is discharged through line 23, while the heavy fraction is passed through line 24 to a second distillation column 25 wherein cyclohexanone is distilled and recovered through line 26. The heavier fraction flows through line 27 to a third distillation column 28. Cyclohexanol is distilled off and if so desired passed through line 29 to a dehydrogenation unit (not shown) where it can be converted into a further amount of cyclohexanone by dehydrogena-

tion in known manner. The dehydrogenation product may be returned to the distillation column through a line (not shown). A distillation residue containing cyclohexyl esters leaves the system through line 30. If so desired the esters may be hydrolyzed, e.g. with aqueous sodium hydroxide, in a hydrolysis reactor (not shown). The cyclohexanol then obtained can be returned through a line not shown into the system, preferably to the neutralization device 6, aldol-condensation reactor 14 or washing device 17.

Instead of a hydroxide solution, an aqueous solution of a strong acid, e.g. 10% by weight sulphuric acid, can be fed in through line 15, or aldol condensation vessel 14 may be a column filled with a strongly acid ion exchanger, e.g. Dowex 50 L (Dowex is a trade-mark), or another polystyrene resin containing sulphonic acid groups and cross-linked with divinyl benzene. In this instance washing device 17 can be omitted.

The invention will be further elucidated with reference to the following working examples and comparative experiments.

A glass reactor provided with baffles, a reflux condenser and a stirrer is filled with a mixture that contains 70 grams of cyclohexanone, 130 grams of cyclohexanol, and 2 grams of aldehydes (substantially caproaldehyde) plus the cyclohexyl esters of butyric acid, valeric acid, caproic acid and adipic acid which has been obtained by oxidation of cyclohexane in liquid phase with air followed by neutralization with aqueous sodium carbonate solution, separation of the layers and removal of unconverted cyclohexane by evaporation (flow in line 13 of the drawing). An aqueous sodium-hydroxide solution is added to this mixture in the amounts and concentrations shown in the accompanying Table and vigorously stirred with reflux cooling for 60 minutes at about 95°C and atmospheric pressure. After completion of the reaction, the contents of cyclohexylidene cyclohexanone, aldehyde (calculated as caproaldehyde) and ester in the organic layer are determined by gas-liquid chromatography (GLC). The results are shown in the table:

Amount and concentration of sodium-hydroxide solution	Degree of conversion % aldehydes cyclohexyl esters	Loss of cyclohexanone % by weight *
Ex. I 20 ml 0.1 N	80 2	< 0.01
Ex. II 20 ml 0.5 N	90 5	0.02
Ex. III 20 ml 1 N	97 10	0.1
Ex. IV 10 ml 1 N	97 10	0.2
Ex. V 20 ml 2.5 N	98 17	0.4
Com. Ex. A 20 ml 7.5 N	> 99 25	1.5
Com. Ex. B 20 ml 10 N	> 99 35	4.2

* calculated to the sum of cyclohexanone and cyclohexanol added

Upon completion of the reaction, pure cyclohexanone can be recovered from this organic layer by distillation.

CLAIMS

1. A process for the purification of a mixture containing a cycloalkanone containing 5-12 carbon atoms in the ring obtained by the oxidation of the corresponding cycloalkane in the liquid phase by means of a gas containing molecular oxygen, characterized in that the said mixture containing the cycloalkanone is subjected to an aldol condensation reaction by which at least 80% of the aldehydes present are converted, but not more than 20% of cycloalkyl esters derived from carboxylic acids containing at least 4 carbon atoms per molecule is allowed to saponify.
2. A process according to Claim 1, wherein not more than 5% of the said cycloalkyl esters is allowed to saponify.
3. A process according to Claim 1 or Claim 2, wherein not more than 0.2% cycloalkanone in excess of that required for the removal of the aldehydes is converted in the aldol condensation reaction.
4. A process according to any of Claims 1 to 4,

wherein a reaction temperature of between 30° and 100°C is used.

5. A process according to any of Claims 1 to 5, wherein a basic catalyst is used.

6. A process according to Claim 5, wherein the reaction temperature is from 60° to 95°C.

7. A process according to Claim 5 or Claim 6, wherein the said basic catalyst is an aqueous solution of sodium hydroxide or sodium carbonate.

8. A process according to any of Claims 5 to 7, wherein the base concentration is not more than 15% by weight.

9. A process according to any of Claims 1 to 4, wherein an acid catalyst is used.

10. A process according to Claim 9, wherein a reaction temperature of from 30° to 60°C is used.

11. A process according to Claim 9 or Claim 10, wherein the said acid catalyst is an aqueous solution of sulphuric acid.

12. A process according to Claim 9 or Claim 10, wherein the said acid catalyst is a strongly acid ion exchanger.

13. A process according to any of Claims 9 to 12, wherein the concentration of the strong acid corresponds to not more than 20% by weight sulphuric

acid.

14. A process according to any of Claims 1 to 13, wherein after the aldol condensation reaction, the cycloalkanone is separated from the resulting condensation products by distillation.

15. A process according to any of Claims 1 to 14, wherein the cycloalkanone is cyclohexanone.

16. A process according to Claim 1, substantially as hereinbefore described and illustrated in the accompanying drawing.

17. A process according to Claim 1, substantially as hereinbefore described in the Examples.

18. Cycloalkanone obtained by a process according to any of Claims 1 to 17.

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Published at the Patent Office, 25 Southampton Buildings, London, WC2A 1AY,
from which copies may be obtained.

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1/2

PATENT SPECIFICATION

(11) 1 276 792

DRAWINGS ATTACHED



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(54) ACETONE PURIFICATION PROCESS

(71) We, ALLIED CHEMICAL CORPORATION, a corporation organised and existing under the laws of the State of New York, United States of America, of 61 Broadway, New York 6, New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

Crude acetone, such as that obtained as a by-product with phenols from the catalytic decomposition of cumene hydroperoxide, generally contains varying quantities of impurities. These impurities are especially difficult to remove from the acetone and yet, if present even in very small amounts, make the acetone unsuitable for numerous uses. For example, the U.S. National Formulary has established tests which acetone must pass in order to be labelled Acetone, NF. One such test is the well-known potassium permanganate test. It is further known that impurities in crude acetone, which are responsible for its failure to pass the permanganate test, include principally aldehydic substances such as propionaldehyde and acetaldehyde. The prior art includes many methods for effecting separation of these aldehydic impurities, most of which depend upon differences in volatilities. In addition to effecting separation of impurities by distillation methods, caustic has been used to facilitate purification. For example, the prior art has suggested that acetone may be purified by first pre-treating the acetone with sodium hydroxide to polymerise the aldehydes to high boiling materials and then subjecting the mixture to distillation. According to other processes, acetone is fed into a distillation column and sodium hydroxide solution is simultaneously injected into the column either above or below or at the same point as the acetone feed. The sodium hydroxide thus catalyses the polymerisation of the aldehydes present, thereby forming non-volatile components which may be withdrawn as bottoms from the column, while pure acetone is withdrawn overhead.

The main disadvantage encountered in the prior art methods is that the polymerisation of aldehydes with caustic under the conditions suggested results either in a reversible process, making removal quite inefficient, or, using more rigorous conditions, in the degradation of a substantial portion of the acetone.

In accordance with the present invention, a process has been found for separating impurities from acetone prepared by the decomposition of the cumene hydroperoxide, which obviates the features of the methods presently being used.

Accordingly, the present invention provides a process for purifying crude acetone obtained by decomposing cumene hydroperoxide, the process comprising fractionally distilling the acetone in a multiple-plate column and continuously adding to the column a dilute aqueous solution of an alkaline material, as hereinafter defined, the solution being added at a point above the acetone feed point and the amount and concentration of the solution being sufficient to polymerize impurities in the acetone without forming a second liquid phase.

It has been found that crude acetone containing aldehydic impurities can be purified to an extent such that it will pass the standard potassium permanganate test, by combination of chemical treatment and distillation, effected in a single, multiple-plate distillation tower. This method of purifying acetone comprises distilling crude acetone to form a vapour phase mixture comprising water, acetone and aldehydic components, such as acetaldehyde and propionaldehyde, further treating this vapour mixture with a counter-flowing dilute solution of an alkaline material, particularly an alkali metal hydroxide, and removing pure acetone from overhead.

The invention may be better understood by referring to Figure 1, which is a schematic flow diagram showing the arrangement of equipment adaptable for continuously per-

forming the method on a commercial scale. The process utilizes a single tower containing multiple plates or trays, Figure 1 illustrating a tower or column with 60 plates, and provided with conventional accessories such as heat source 6 for supplying heat, for example, in the form of steam to the bottom of the column, condenser 9, for condensing the vapours leaving the column, outlet 8, for withdrawing non-volatile components from the bottom of the column, feed inlet F1, for feeding crude acetone to the column, feed inlet F2, for feeding a dilute aqueous solution of alkaline material through the column, pipe 3 for conveying overhead vapours to the condenser, pipe 4 for returning a portion of the condensed vapour to the column for reflux, and pipe 5 for withdrawing product. Plates 1, 7, 17, 57 and 60 represent a portion of the plates dispersed within the column; other plates are omitted for simplicity. The portion of the column between F1 and F2 is designated as the reaction zone.

Crude acetone is fed into the column through feed inlet F1 located in the lower section of the column about 7 to 10 plates above the steam source and below the alkali feed inlet F2, which is located about 15 or 20 plates above the bottom of the column. The alkali mixes with the downflowing liquid in the column forming a single, acetone-rich liquid phase which contacts the upflowing vapours of acetone and aldehydes, converting the aldehydes to non-volatile polymers which tend to settle in the bottom of the column with water and the spent alkali, and which are removed through outlet 8. The rising vapours, now containing acetone and a small amount of water, are continuously rectified in the uppermost portion of the column, the vapour leaving the column above plate 60 through pipe 3 to condenser 9 and a portion of the condensate returned to the upper rectification zone through pipe 4. The other portion of the condensate, free of water, is withdrawn as refined product through pipe 5.

The term, "acetone substantially free of water", as used herein, means acetone containing less than 0.5% water.

When sodium hydroxide, acetone and water are mixed together, depending on the relative proportions of each present, the resulting solution may contain two phases, wherein the less dense liquid is known as the acetone-rich phase, and the more dense liquid is known as the alkali-rich phase, or the mixture may contain one, acetone-rich phase. Figure 2 illustrates this phase relationship; mixtures containing acetone, water and sodium hydroxide in the proportions represented by the region below the curve form two phases and within the shaded area, a single acetone-rich phase.

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We have found that aldehydic impurities can best be removed in a distillation column using an alkaline material as a polymerisation catalyst and under conditions wherein a single acetone-rich phase is formed in the reaction zone of the column.

By "alkaline material" as used herein is meant any inorganic basic material which is soluble in the acetone-rich liquid and will polymerise the aldehydes present. Suitable materials include alkaline earth metal oxides and hydroxides, and alkali metal oxides, carbonates and hydroxides, but preferably alkali metal hydroxides, e.g. sodium and potassium hydroxide are used.

The presence of a single acetone-rich liquid phase is important in that polymerisation is dependent on the aldehydic impurities entering the liquid phase, and the latter is only possible if the liquid is rich in acetone, since the impurities are more soluble in acetone than water. The presence of a second liquid phase is to be avoided, since this would tend to reduce the column hold-up or residence time of the acetone-rich liquid phase. In addition, a second liquid phase, which is rich in caustic and poor in acetone, would tend also to polymerise and degrade acetone without effectively removing the aldehydes present.

Thus, in effecting separation of the aldehydic impurities from the crude acetone according to the process described above, an alkaline material, preferably sodium hydroxide or potassium hydroxide, is fed to the column at a rate and concentration sufficient to promote polymerisation of aldehydes present without forming a second liquid phase in the reaction mixture. Accordingly in order to efficiently effect polymerisation without forming a second phase, it is necessary that the alkaline material be introduced in a dilute, (preferably 0.05 to 5.0%, the range 0.2 to 1.0% being especially preferred) solution and in an amount in relationship to the acetone and water already present in the column such that a single liquid phase is maintained. All solution concentrations herein are expressed on a weight/weight basis.

The relative feed rate of acetone and alkali necessary in order to maintain a single acetone-rich liquid phase in the reaction zone will vary depending on the reflux rate and the concentration of alkali used. In a preferred embodiment of our invention, we find that purification may be suitably effected when the ratio of caustic feed rate to reflux rate is from 1:2 to 1:10, depending on the caustic concentration, and preferably 1:3.3 to 1:6.

As will be appreciated by those skilled in the art, the required reflux ratio is determined by the desired dryness of the refined acetone. For commercially dry acetone,

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reflux ratios ranging from 2.1:1 to 3:1 are used.

Although the method described above illustrates the invention utilising a column having 60 trays, modification of the column to contain more or less than 60 trays may be made in order to vary the efficiency of the system. Similarly, the plates placed within the column may be of conventional construction or design, such as the perforated or the overflow type, the limiting factor being the number and capacity necessary to afford proper contact between the rising vapour phase and the counter-flowing liquid phase in the reflux mixture.

The following Examples further illustrate the invention.

EXAMPLE 1

Acetone was purified by continuously distilling in a three-section distillation column (25 mm in diameter) comprising a vacuum jacketed 15-plate Oldershaw central section and a packed upper section, representing 10 theoretical trays, and a packed lower section, representing 15 theoretical trays. Steam was passed into the bottom of the lower packed column, and crude acetone was fed at the bottom of the Oldershaw section at a rate of 2.4 grams/minute.

An aqueous 0.5% solution of sodium hydroxide was fed into the top of the Oldershaw section above the acetone feed at a rate of 2.4 grams/minute and the distillation carried out continuously at a reflux ratio of 2.3:1.

Bottom liquid was withdrawn at a rate of 4.71 grams/minute. This system was continuously operated for 35 hours, and samples of the acetone obtained from the overhead condensate were periodically tested for purity.

Table I, below, indicates the purity of acetone withdrawn from the top of the column.

TABLE I

Sample	Hours of Operation	Acetaldehyde ppm	Propionaldehyde ppm
Crude Acetone		258	80
1	2	3	trace
2	10	3	trace
3	20	5	1
4	33	4	1

EXAMPLE 2

Crude acetone was continuously distilled at a reflux ratio of 3:1 in a 30-plate column (two 15-plate Oldershaw sections) equipped

with a condensing unit at the top of the column and a bottom withdrawal and steam inlet at the bottom by introducing:

- acetone containing 522 ppm of acetaldehyde and 228 ppm of propionaldehyde at a point near plate 15; and
- 0.1% sodium hydroxide at a point near plate 30 of the column, the feed ratio of acetone to sodium hydroxide being 1.4:1.

The vapours leaving the top of the column were condensed and a portion returned to the top of the column as reflux. The acetone condensate thus collected, when analysed by gas chromatography, was found to contain 10 ppm of acetaldehyde and 5 ppm of propionaldehyde.

When the procedure was repeated using 1% sodium hydroxide and the acetone: sodium hydroxide feed ratio was 1:1, the acetone obtained from the overhead condensate had less than 0.3 ppm of acetaldehyde and propionaldehyde.

WHAT WE CLAIM IS:—

1. A process for purifying crude acetone obtained by decomposing cumene hydroperoxide, the process comprising fractionally distilling the acetone in a multiple-plate column and continuously adding to the column a dilute aqueous solution of an alkaline material, as hereinbefore defined, the solution being added at a point above the acetone feed point and the amount and concentration of the solution being sufficient to polymerize impurities in the acetone without forming a second liquid phase.

2. A process according to Claim 1, wherein the concentration of the solution of alkaline material is 0.2 to 1.0% w/w.

3. A process according to Claim 1 or 2 wherein the alkaline material is an alkali metal hydroxide.

4. A process according to Claim 3, wherein the alkali metal hydroxide is sodium or potassium hydroxide.

5. A process according to any one of the preceding claims, wherein the ratio of the rate of adding the solution of alkaline material to the reflux rate is 1:3.3 to 1:6.

6. A process according to Claim 1 substantially as described herein.

7. Acetone purified by a process according to any one of the preceding claims.

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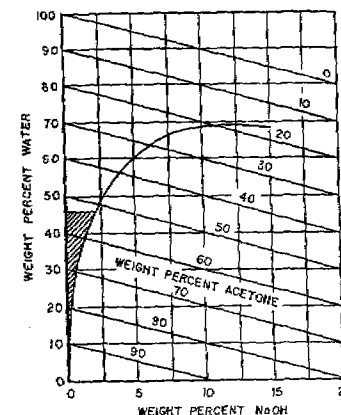


FIG. 2

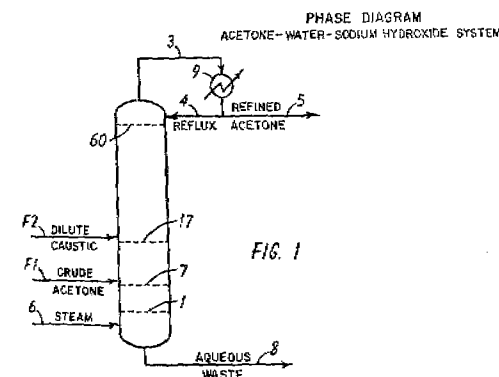


FIG. 1