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(54) Title: CATALYTIC VAPOR PHASE PROCESS FOR PRODUCING DIHYDROCARBYL CARBONATES

(57) Abstract

A process for the preparation of dihydrocarbyl carbonates comprising contacting an alkanol, carbon monoxide and oxygen with a heterogeneous catalyst which comprises a metal halide or mixed metal halide impregnated on an appropriate support and a process for reactivating the heterogeneous metal halide catalyst which comprises drying and then contacting the supported catalyst with a gaseous stream of hydrogen halide.

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CATALYTIC VAPOR PHASE PROCESS FOR PRODUCING DIHYDROCARBYL CARBONATES

This invention relates to the carbonylation of alkanols. More specifically, it pertains to a process for carbonylating alkanols in the vapor phase in the presence of a heterogeneous catalyst to produce dihydrocarbyl carbonates.

This invention also relates to a method for reactivating the heterogeneous catalyst used in the above process for carbonylating alkanols in the vapor phase to produce dihydrocarbyl carbonates.

The carbonates produced by this invention are well-known and are useful as synthetic lubricants, solvents and chemical intermediates in the preparation of polymeric derivatives such as clear plastics.

The traditional method for producing carbonates involves contacting phosgene with an appropriate alcohol. See Drake et al., J. Am. Chem. Soc., 52, 3720 (1960) and U.S. Patent 2,379,250. This method results in the production of hydrogen chloride and thereby

leads to the undesirable production of chlorine-containing by-products. In particular, the use of secondary alcohols leads to a significant formation of alkyl chlorides. Attempts to neutralize the hydrogen chloride have led to processing difficulties.

Other methods of producing carbonates generally involve the homogeneous liquid phase reaction of an alkanol, carbon monoxide and oxygen in the presence of a catalyst. For example, U.S. Patent 4,360,477 describes a method for carbonylating alkanols with carbon monoxide and oxygen at elevated temperatures in the presence of copper salts. U.S. Patent 4,370,275 discloses a process for preparing carbonates by reacting an alcohol, carbon monoxide and oxygen in the presence of a catalyst system containing copper, chemically bonded oxygen, chemically bonded halogen and at least one nitrogen base. The oxidative carbonylation process claimed in U.S. Patent 4,426,331 involves the reaction of carbon monoxide, oxygen and an alcohol in the presence of a copper compound and a sulfone. U.S. Patent 4,218,391 indicates that high acidity in carbonylation reactions involving metal salts leads to significant formation of by-products. U.S. Patent 3,980,690 describes a carboxylation, in the heterogeneous phase, using a catalyst system consisting of a polymer bound to a metal by a coordinate bond.

The above processes utilizing a homogeneous process require elaborate separation techniques to separate the organic base promoter in the azeotropic mixtures which can form between the dialkyl carbonate and the by-product water or unreacted alkanol. In addition, complex distillation steps are necessary to recover the catalysts for recycle to the processes.

Due to the highly corrosive nature of most solutions containing copper halides and alkanols, expensive materials of construction are required for the reaction vessels and pipelines.

The above processes also do not provide for an efficient method of regenerating the catalysts used therein. Most catalysts can be regenerated by being subjected to acidic conditions. However, highly acidic conditions in the actual reaction mixture can lead to significant by-product formation. Therefore, over-acidification of the catalyst can lead to lower selectivities.

A process for the catalytic production of dihydrocarbyl carbonates is needed that would eliminate the above problems regarding separation and distillation and that would facilitate the regeneration of the catalyst utilized. An efficient method for regenerating the catalyst is also needed that would not interfere with the selectivity of the catalyst.

The present invention provides such a process for the production of dihydrocarbyl carbonates and avoids many of the problems heretofore encountered. The process of the present invention comprises reacting oxygen, carbon monoxide and an alkanol, all in the vapor phase, in the presence of a heterogeneous catalyst containing a metal halide or a mixed metal halide impregnated on an appropriate support under reaction conditions sufficient to produce a dihydrocarbyl carbonate.

This heterogeneous process effectively eliminates the need for elaborate separation techniques

and complex distillation steps which were heretofore necessary in order to separate the catalyst from the reaction product. The supported catalyst is easily regenerated and the process can be carried out under relatively mild conditions while minimizing the production of unwanted by-products. Furthermore, no organic base promoter, such as pyridine, is needed since the support serves this function.

The supported heterogeneous catalyst used in the aforementioned carbonylation reaction can also be reactivated. The regeneration method comprises drying and contacting the catalyst with a gaseous stream of hydrogen halide for a period of time which is sufficient to convert all of the metal present to the corresponding metal halide. This regeneration process unexpectedly allows the carbonylation catalyst to be treated under strongly acidic conditions without adversely affecting the performance and selectivity of the catalyst.

The metal halide useful in the practice of the present invention can be any metal halide that will effectively catalyze the carbonylation reaction contemplated herein. The metal is preferably selected from the metals in Groups VIIIA or IB. Preferred metals include copper, nickel, iron and cobalt. The metal is most preferably copper. The halide can be chloride, bromide, iodide or fluoride and is most preferably chloride. Preferred metal halides include cupric chloride, nickel chloride and iron chloride with cupric chloride being most preferred.

Mixed metal halide herein refers to a combination of the metal halide described above with a

second metal halide. The metal of the second metal halide is selected from Groups IA or IIA. Typical metals that can be used in the second metal halide of the present invention include potassium, sodium, lithium, magnesium, cesium and calcium. The metal is preferably selected from Group IA with potassium being the most preferred metal. The halide can be chloride, bromide, iodide or fluoride and is most preferably chloride. Preferred mixed metal halides include cupric chloride/potassium chloride and cupric chloride/-magnesium chloride with cupric chloride/potassium chloride being most preferred.

Any support which will withstand the carbonylation conditions described herein can be used in the process of the present invention. Typical appropriate supports include the well-known carbon supports such as activated carbon, carbon black, chars and coke. Other supports may also be used such as alumina, titania, silicon carbide, silica or mixtures thereof. A carbon support is generally preferred, with activated carbon being the most preferred support. The use of activated carbon as a support results in a significantly higher rate of reaction than the use of other commonly known supports. Furthermore, the selectivity of the reaction toward the dihydrocarbyl carbonate based on the amount of carbon monoxide fed to the reaction is higher when activated carbon is used as the support in comparison to other commonly used supports. An acid-washed lignite activated carbon having a particle size in the range from 0.85 to 1.70 mm is particularly active in the process of the present invention.

The metal halide may be supported on the carrier material by any standard impregnation technique such as that disclosed in Experimental Methods in Catalytic Research, Vol. II, edited by R. B. Anderson and P. T. Dawson, Academic Press, New York, 1978. In the case of a mixed metal halide, the two metal halides may be mixed together and impregnated onto the support simultaneously or the metal halides may be impregnated separately.

Alcohols useful in this invention include any alcohol which is vaporizable under the reaction conditions. Preferred alcohols correspond to the formula R^1OH wherein R^1 is C_{1-6} alkyl, C_{3-6} cycloalkyl, or benzyl or mixtures thereof. R^1 is preferably C_{1-6} alkyl, more preferably methyl, ethyl or propyl, and most preferably methyl.

Preferred alcohols include methanol, ethanol, propanol, butanol, pentanol, hexanol, cyclopropanol, cyclobutanol, cyclopentanol, cyclohexanol and benzyl alcohol. More preferred alcohols are methanol, ethanol, propanol, butanol, pentanol and hexanol. Even more preferred alcohols are methanol, ethanol or propanol, with methanol being most preferred.

This process prepares dihydrocarbyl carbonates, wherein the hydrocarbyl moiety corresponds to the hydrocarbon portion of the alcohol used in the preparation. Preferred carbonates correspond to the formula

$$R^1O\text{-}\overset{\overset{O}{\|}}{C}\text{-}OR^1$$

wherein R^1 is C_{1-6} alkyl, C_{3-6} cycloalkyl, or benzyl. R^1 is preferably C_{1-6} alkyl, more preferably methyl, ethyl or propyl, and most preferably methyl.

Examples of carbonates prepared by this invention include dimethyl carbonate, diethyl carbonate, dipropyl carbonate, dibutyl carbonate, dipentyl carbonate, dihexyl carbonate, dicyclopropyl carbonate, dicyclobutyl carbonate, dicyclopentyl carbonate, dicyclohexyl carbonate, dibenzyl carbonate, methylethyl carbonate, ethylpropyl carbonate, methylpropyl carbonate and the like. Preferred carbonates prepared by this process include dimethyl carbonate, diethyl carbonate, dipropyl carbonate, dibutyl carbonate, dipentyl carbonate and dihexyl carbonate. Even more preferred carbonates are dimethyl carbonate, diethyl carbonate and dipropyl carbonate. The most preferred carbonate prepared by this invention is dimethyl carbonate.

In general, the alcohol or mixture of alcohols is contacted with oxygen and carbon monoxide under carbonylation conditions so as to prepare a carbonate. In the embodiment wherein a mixture of alcohols is used, the carbonates prepared are a mixture of symmetrical and unsymmetrical carbonates. When a single alcohol is used, the product is a symmetrical carbonate. The symmetrical dihydrocarbyl carbonates are the preferred carbonates.

The process of this invention involves contacting carbon monoxide, oxygen and an alcohol in the vapor phase and passing them over the supported

metal halide described hereinbefore. The process of this invention can be illustrated by the equation

$$2R^1OH + \tfrac{1}{2}\,O_2 + CO \rightarrow R^1\text{-}O\overset{\overset{O}{\|}}{C}\text{-}O\text{-}R^1 + H_2O$$

wherein R^1 is as defined hereinbefore. The ratio of carbon monoxide to the alcohol can be any mole ratio which results in the preparation of the dihydrocarbyl carbonates. Preferably, the ratio of carbon monoxide to the alcohol is between 1:1 and 1000:1 moles. More preferably, the ratio of carbon monoxide to alcohol is between 1:1 and 100:1 moles, and most preferably the ratio of carbon monoxide to alcohol is between 1:1 and 10:1 moles. The ratio of oxygen to alcohols is any ratio which results in the preparation of the dihydrocarbyl carbonates. Preferably, the ratio of oxygen to alcohol is between 1:1 and 1:1000 moles. More preferably the ratio of oxygen to alcohol is between 1:1 and 1:100 moles. Most preferably the ratio of oxygen to alcohol is between 1:1 and 1:10 moles. The ratio of oxygen to carbon monoxide is any ratio which results in the preparation of the dihydrocarbyl carbonates. Preferably, the ratio of oxygen to carbon monoxide is between 1:1 and 1:1000 moles. More preferably the ratio of oxygen to carbon monoxide is between 1:1 and 1:100 moles, and most preferably the ratio of oxygen to carbon monoxide is between 1:1 and 1:10 moles.

The oxygen can be added to the reaction mixture as pure molecular oxygen or diluted with an inert gas

such as nitrogen or argon. It is preferred to keep the oxygen concentration at no more than 10 mole percent of the entire reaction feed so as to avoid the formation of explosive mixtures.

This process can be performed at any temperature and pressure at which the reaction proceeds. Preferred temperatures are between 20°C and 150°C, with between 90°C and 125°C being more preferred. The most preferred temperatures are between 115°C and 125°C. The pressure can be atmospheric or superatmospheric pressure. Preferred pressures are between 1 and 100 atmospheres, with between 15 and 25 atmospheres being most preferred.

The reaction mixture feed gas flow rate expressed as gas hourly space velocity can be between 100 and 50,000 (Hr^{-1}), and most preferably between 1,000 and 2,000 (Hr^{-1}). The dihydrocarbyl carbonate can be recovered from the reaction mixture by methods well-known in the art, one particularly desirable method is the use of extractive distillation of the condensed reaction product.

The process of this invention can be performed in either a fixed or fluid bed reactor using either continuous or batch processing methods. It is preferred to use a fixed bed reactor and a continuous mode of operation. Preferably, from 5×10^{-5} to 2.3×10^{-4} moles of dihydrocarbyl carbonate are produced per gram atom of metal per second. In the case of a mixed metal halide, the metal of the second metal halide is not considered in determining reaction rate. Selec-

tivities based on the alcohol preferably range from 75 to 85 percent.

The method for the regeneration of the catalyst hereinbefore described provides a sequence of catalyst treatment steps comprising drying and contacting the catalyst with a gaseous stream of hydrogen halide, preferably diluted with an inert gas, at a sufficient temperature and for a sufficient period of time to convert all of the metal present to the metal halide.

The regeneration process basically comprises two major steps. The first step comprises heating the catalyst in the presence of an inert gas at a sufficient temperature and for a sufficient amount of time so as to remove moisture. The second step involves subjecting the dried catalyst to gaseous hydrogen halide which has preferably been diluted with an inert gas or air for a sufficient amount of time and at an appropriate temperature to effectively reactivate the catalyst.

Typical inert gases useful in the present invention include nitrogen, helium and argon, with nitrogen and helium being preferred. The most preferred inert gas for the first step is nitrogen. Air is most preferred for the second step for reasons of convenience and economy.

The first or drying step can be carried out at any temperature sufficient to effectively remove a substantial amount of moisture from the catalyst. The precise amount of moisture removed from the catalyst is not critical but should be an amount sufficient to prevent substantial interference with catalytic

activity. Typical drying temperatures range from 90 to 300°C, with 115 to 140°C being preferred. Typical first step drying times range from 0.1 to 24 hours, with 2 to 4 hours being preferred. The first step can be carried out at any pressure sufficient for elimination of moisture. Typical pressures range from 0.1 to 500 psi with atmospheric pressure being preferred for convenience. The inert gas flow rate can range from between 0.025 to 250 cc (STP) per cc of catalyst per hour. Preferably, the inert gas flow rate ranges between 10 and 50 cc (STP) per cc of catalyst per hour, with 30 cc (STP) per cc of catalyst per hour being most preferred.

The hydrohalogenation step can be carried out at any temperature sufficient to reactivate the catalyst. Typical temperatures range from ambient temperature to 300°C and preferably range from 110 to 150°C. The catalyst is subjected to hydrohalogenation from between 0.1 to 24 hours with between 0.5 and 2 hours being preferred. Typical pressures involved in the hydrohalogenation step range between 0.1 to 500 psi with atmospheric again being preferred for convenience. The typical gas flow rates in the hydrohalogenation step range from between 0.025 to 250 cc (STP) per cc of catalyst per hour with between 20 and 60 cc (STP) per cc of catalyst per hour being preferred. When an inert gas or air is used to dilute the hydrogen halide, the hydrogen halide is present in the inert gas or air in concentrations ranging from 0.1 to 99 mole percent based on the inert gas or air, with between 5 and 20 mole percent of hydrogen halide being preferred.

The following examples are included for the purposes of illustration only and are not to be

construed to limit the scope of the invention. Unless otherwise indicated, all parts and percentages are by weight.

Example 1

On a commercial activated carbon (DARCO®, 20 g, 0.85-1.70 mm) is supported 2.5 g of $CuCl_2$ from an ethanol solution by standard impregnation techniques. The dried catalyst is analyzed as 4.37 weight percent copper. Into a ½-inch (1.3 cm) outside diameter flow reactor operated at 115°C and at 20 atm pressure is loaded 1.6 g of catalyst. A flow consisting of 80 cc (STP) per minute of CO and 13 cc (STP) per minute of oxygen is passed through the reactor. Liquid methanol is fed to a vaporizer operated at 185°C with an LC pump which allows small amounts of CH_3OH to be added to the system under pressure. A flow of CH_3OH vapor of 30 cc (STP) per minute is introduced into the CO/O_2 feed stream prior to flowing through the reactor. The reaction products are continuously monitored on-line by standard gas chromatography techniques. Dimethyl carbonate is produced at a rate of 5.3 to 5.5 x 10^{-4} moles per gram atom of copper per second with 80 percent selectivity based on methanol.

Example 2

The reactor in Example 1 is purged with nitrogen and cooled to room temperature. The catalyst of Example 1 is heated to 125°C in nitrogen (125 cc STP per minute) and held at that temperature for 2 hours to remove moisture. The catalyst is chlorinated by passing a mixture of 10 percent HCl/90 percent N_2 (175 cc STP per minute) through the reactor for 3 hours and

then cooling the catalyst to room temperature while maintaining the HCl/N_2 flow. The reactivated catalyst exhibits an activity of 5.1×10^{-4} moles of dimethyl carbonate per gram atom of copper per second, indicating that the activity of the aged catalyst is almost completely returned to that of the fresh catalyst.

CLAIMS

1. A process comprising reacting oxygen, carbon monoxide and an alkanol, all in the vapor phase, in the presence of a heterogeneous catalyst containing a metal halide or a mixed metal halide impregnated on an appropriate support under reaction conditions sufficient to produce a dihydrocarbyl carbonate.

2. The process of Claim 1 wherein the alkanol is a C_{1-6} alkanol, a C_{3-6} cycloalkanol or benzyl alcohol, or mixtures thereof, and the hydrocarbyl groups on the dihydrocarbyl carbonate are separately in each occurrence C_{1-6} alkyl, C_{3-6} cycloalkyl or benzyl.

3. The process of Claim 2 wherein one alkanol is used and the dihydrocarbyl carbonate prepared is symmetrical.

4. The process of Claim 3 wherein the alkanol is a C_{1-6} alkanol and the dihydrocarbyl carbonate is a C_{1-6} dialkyl carbonate.

5. The process of Claim 4 wherein the alkanol is methanol and the dihydrocarbyl carbonate is dimethyl carbonate.

6. The process of any one of Claims 1 to 5 wherein the metal halide is a copper, nickel, iron or cobalt halide.

7. The process of Claim 6 wherein the halide is a chloride.

8. The process of Claim 7 wherein the halide is cupric chloride.

9. The process of any one of Claims 1 to 5 wherein the mixed metal halide consists of cupric chloride and potassium, sodium, lithium, magnesium, cesium or calcium chloride.

10. The process of Claim 9 wherein the mixed metal halide consists of cupic chloride and potassium chloride.

11. The process of Claim 1 or 8 wherein the support is activated carbon.

12. The process of Claim 11 wherein the activated carbon is an acid-washed lignite carbon.

13. The process of Claim 1 wherein the ratio of carbon monoxide to alcohol is between 1:1 and 10:1; the ratio of oxygen to alcohol is between 1:1 and 1:10.

14. The process of Claim 1 wherein the temperature is between 20 to 150°C.

15. The process of Claim 1 wherein the pressure is between 1 and 100 atmospheres.

16. A process for reactivating supported heterogeneous metal halide or mixed metal halide catalysts as defined in any one of Claims 1 to 15, comprising drying and then contacting the supported catalyst with a gaseous stream of hydrogen halide for a period of time which is sufficient to convert all of the metal present to the corresponding metal halide.

AMENDED CLAIMS

[received by the International Bureau on 09 November 1987 (09.11.87);
original claims 11,12 and 16 amended, other claims unchanged (2 pages)]

6. The process of any one of Claims 1 to 5 wherein the metal halide is a copper, nickel, iron or cobalt halide.

7. The process of Claim 6 wherein the halide is a chloride.

8. The process of Claim 7 wherein the halide is cupric chloride.

9. The process of any one of Claims 1 to 5 wherein the mixed metal halide consists of cupric chloride and potassium, sodium, lithium, magnesium, cesium or calcium chloride.

10. The process of Claim 9 wherein the mixed metal halide consists of cupic chloride and potassium chloride.

11. The process of Claim 1 wherein the support is activated carbon.

12. The process of Claim 11 wherein the activated carbon is an acid-washed lignite carbon.

13. The process of Claim 1 wherein the ratio of carbon monoxide to alcohol is between 1:1 and 10:1; the ratio of oxygen to alcohol is between 1:1 and 1:10.

14. The process of Claim 1 wherein the temperature is between 20 to 150°C.

15. The process of Claim 1 wherein the pressure is between 1 and 100 atmospheres.

16. A process for reactivating supported heterogeneous metal halide or mixed metal halide catalysts containing a metal halide or a mixed metal halide impregnated on an appropriate support under reaction conditions sufficient to produce a dihydrocarbyl carbonate, comprising drying and then contacting the supported catalyst with a gaseous stream of hydrogen halide for a period of time which is sufficient to convert all of the metal present to the corresponding metal halide.

INTERNATIONAL SEARCH REPORT

International Application No PCT/US87/01309

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [3]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC(4): C07C 67/36, 69/96; B01J 38/42, 38/44

U.S. Cl.: 558/260, 275, 277; 502/35, 37

II. FIELDS SEARCHED

Minimum Documentation Searched [4]

Classification System	Classification Symbols
U.S.	558/260, 275,277; 502/35, 37

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [6]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [14]

Category *	Citation of Document, [16] with indication, where appropriate, of the relevant passages [17]	Relevant to Claim No. [18]
X	U.S., A, 3,980,690 (CIPRIANI) 14 September 1976. See the entire document.	1-10, 13-15
Y	U.S., A, 1,848,723 (JAEGER) 8 March 1932. See page 1, lines 77-100; page 2, lines 6-9 and 57-61; claims 1 and 5.	16
Y	U.S., A, 3,479,392 (STERN) 18 November 1969. See column 7, lines 68-75 and column 8, lines 1-7.	16
A	U.S., A, 4,361,519 (HALLGREN) 30 November 1982. See claim 1.	1-10, 13-15
A	U.S., A, 3,846,468 (PERROTTI) 05 November 1974. See claim 1.	1-10, 13-15

* Special categories of cited documents: [15]

"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

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search [2]	Date of Mailing of this International Search Report [2]
27 AUGUST 1987	21 SEP 1987
International Searching Authority [1]	Signature of Authorized Officer [20]
ISA/US	Vivian Garner Vivian Garner

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

A	U.S., A, 3,952,045 (GAENZLER) 20 April 1976. See claim 1.	1-10, 13-15
A	U.S., A, 2,113,028 (KUENTZEL) 05 April 1938. See column 1, lines 23-30 and column 3, lines 3-69.	16
A	U.S., A, 4,069,268 (SISKIN) 17 January 1978. See claim 1.	16

V. ☐ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE [10]

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1. ☐ Claim numbers . because they relate to subject matter [12] not required to be searched by this Authority, namely:

2. ☒ Claim numbers 11-12 because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out [13], specifically:

Claims 11-12 are improper multiple dependent claims because they depend indirectly from claim 6 which is also a multiple dependent claim. PCT Rule 6.4(a); Article 17(2)(b).

VI. ☒ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING [11]

This International Searching Authority found multiple inventions in this international application as follows:

See Attachment.

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application. Telephone Practice.

2. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:

3. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:

4. ☐ As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

Remark on Protest

☐ The additional search fees were accompanied by applicant's protest.

☐ No protest accompanied the payment of additional search fees.

PCT/US87/01309

VI. OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING (ATTACHMENT)

I. Claims 1-15 drawn to a process for preparing dihydrocarbyl carbonates; Class 558, subclass 277.

II. Claim 16 drawn to a process for reactivating supported metal halide or mixed metal halide catalysts; Class 502, subclass 35.

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category *	Citation of Document, [16] with indication, where appropriate, of the relevant passages [17]	Relevant to Claim No [18]
A	CA, A, 615,379 (ENGEL) 28 February 1961. See claim 1.	16
A	Journal Organic Chemistry, Volume 35, issued September 1970 (American Chemical Society-Publishing Division, Easton, Pennsylvania, USA) Takena Saegusa, "Reaction of Cupric Alkoxide and Carbon Monoxide". See page 2976, column 2 to page 2977, column 1 and page 2978, column 1.	1-10, 13-15

PCT/US87/01309

Attachment to Form PCT/ISA/210, Part VI. 1.

Telephone approval:

$140 payment approved by Karen K. Kimble on 27 August 1987 for Group II in a conversation with examiner V. Garner; charge to Deposit Account No. 04-1512. Counsel advised that she has no right to protest for any group not paid for and that any protest must be filed no later than 15 days from the date of mailing of the search report (Form 210).

Reasons for holding lack of unity of invention:

The invention as defined by Group I (claims 1-15) is drawn to a process for preparing dihydrocarbyl carbonates which is classified in Class 558, subclass 277 and which does not require or include the process for reactivating a metal halide catalyst defined by Group II (claim 16) classified in Class 502, subclass 35. The invention of Group I represents a process of using a product (a supported metal halide catalyst) and Group II is a process of making the supported metal halide product. There is no claim to the supported metal halide product to link the inventions of Group I and Group II.

Time Limit for Filing a Protest

Applicant is hereby given 15 days from the mailing of this Search Report in which to file a protest of the holding of lack of unity of invention. In accordance with PCT Rule 40.2, applicant may protest the holding of lack of unity only with respect to the group(s) paid for.