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CAVELIER
ABOGADOS

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SUPERINTENDENCIA Y COMERCIO 1995

Señora Jefe de la
DIVISION DE NUEVAS CREACIONES
SUPERINTENDENCIA DE INDUSTRIA Y COMER
E. S.

Radicación : 00051465 00000002 Folios: 53
Fecha (A/D): 2000-10-10 10:50:26
Trámite : 002 PATENTES D 1 REGISTRO/ 329 COMPLEMEN
Dependencia: 2020 INDUSTRIA Y COMERCIO

Referencia : Expediente No. 00.051.465

Solicitante : **THE DOW CHEMICAL COMPANY**

Asunto : Solicitud de patente para: "POLIMERIZACIÓN
DE OXIDOS DE ALQUILENO SOBRE
INICIALIZADORES FUNCIONALIZADOS"

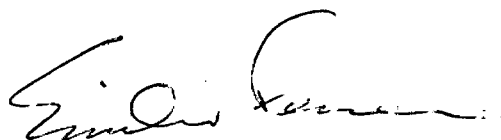
Fecha de solicitud : 10 de julio de 2000

TRAMITE: 002 - EVENTO: 001 - ACTUACIÓN: 329

1. Yo, Emilio FERRERO, obrando como apoderado de la solicitud en referencia, atentamente presento con este escrito las copias certificadas de la solicitudes de patente estadounidenses No. 60,143,081; 60/143,079; 60/143,082 y 60/205,718; del 09 de julio de 1999 las tres primeras, y del 19 de mayo de 2000 la última, junto con sus respectivas traducciones de sus reivindicaciones y certificaciones, de las cuales se reclama prioridad en esta solicitud de patente.

2. Ruego a la Señora Jefe se sirva aceptar este escrito con sus anexos, y se continúe con el trámite de la solicitud.

Bogotá, 10 JUL 2000
Señora Jefe,



EMILIO FERRERO

T.P.A. No. 31.929

COLO 00286-801-125-1
MRE-1545

PA 289118

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00053

THE UNITED STATES OF AMERICA

TO ALL TO WHOM THESE PRESENTS SHALL COME:

UNITED STATES DEPARTMENT OF COMMERCE

United States Patent and Trademark Office

August 14, 2000

**THIS IS TO CERTIFY THAT ANNEXED HERETO IS A TRUE COPY FROM
THE RECORDS OF THE UNITED STATES PATENT AND TRADEMARK
OFFICE OF THOSE PAPERS OF THE BELOW IDENTIFIED PATENT
APPLICATION THAT MET THE REQUIREMENTS TO BE GRANTED A
FILING DATE UNDER 35 USC 111.**

APPLICATION NUMBER: 60/143,079

FILING DATE: July 09, 1999



**By Authority of the
COMMISSIONER OF PATENTS AND TRADEMARKS**

P. R. Grant

P. R. GRANT

Certifying Officer

DISCLOSURE OF INVENTION TO PATENT DEPARTMENT
THE DOW CHEMICAL COMPANY

67

00078

Approval of Department Head
Project No.:

Please fill out carefully. The requested information is needed for proper preparation of a patent application.

You are requested to use only the space provided to describe your invention and to attach additional pages only if necessary.

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Disclosure No.	600725
Assigned to:	Date

However, please attach any report which might prove beneficial in describing or understanding your invention. Call your Patent Department if you have a question.

DOW
CONFIDENTIAL

TITLE OF INVENTION OR DISCOVERY: Process for Preparing Polyethers with reactive substituents

Persons submitting this Disclosure of Invention:

I. Name (Please type or print):			
First	Katherine	Middle	S. Last Clement
Home Address	115 Poinciana		
City	Lake Jackson	County/Parish	Brazoria
State	Texas	Zip Code	77566
Citizenship	USA		
Occupation/Profession	Chemist		
Division	Texas	Bldg.	B-1215
Department	Materials Research & Synthesis	Lab Code	1260
Phone	409-297-2295	Master No.	144988
Signature			

II. Name (Please type or print):			
First	Louis	Middle	L. Last Walker
Home Address	246 Barbara Drive		
City	Clute	County/Parish	Brazoria
State	Texas	Zip Code	77531
Citizenship	USA		
Occupation/Profession	Technologist		
Division	Texas	Bldg.	B-1215
Department	Materials Research & Synthesis	Lab Code	1260
Phone	409-238-9815	Master No.	139939
Signature			

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City	Angleton	County/Parish	Brazoria
State	Texas	Zip Code	77515
Citizenship	USA		
Occupation/Profession	chemist		
Division	Texas	Bldg.	B-4810
Department	Polyglycols TS&D	Lab Code	1054
Phone	409-238-3873	Master No.	140999
Signature			

IV. Name (Please type or print):			
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Home Address	55 North Calla Lilly Ct.		
City	Lake Jackson	County/Parish	Brazoria
State	Texas	Zip Code	77566
Citizenship	USA		
Occupation/Profession	chemist		
Division	Texas	Bldg.	B-4810
Department	Polyglycols R&D	Lab Code	1054
Phone	409-238-4613	Master No.	143727
Signature			

Was this invention made or completed in the course of work under a contract with any governmental agency or other outside party?

YES

NO

If YES, please identify the party and the contract

Witness:

I have read and understood this Disclosure and attachments.

My initials and date are included on all pages attached to this disclosure.

Type or print name of Witness

Signature

Date

DESCRIPTION OF THE INVENTION

00071 68

1

Give a summary/abstract of the Invention: The polyoxide polymerization process using KOH as the catalyst cannot be used with initiators which contain base sensitive functionality such as alkyne, halogen, ester, ketones, aldehydes, alkynes, lactones and acids. Normal acid catalysis allow for the use of base sensitive functionalities but acid catalyzed polyol processes are generally disadvantaged in that the products have broader polydispersities and cyclic by-products are produced. In this invention, double metal cyanide catalysts are used for polymerizing oxides onto initiators containing base sensitive groups such as halogen, ester, ketone, aldehyde, alkyne, lactone and acid. The resulting functionalized polyoxide can be used as is or converted to other products by functional group manipulation. For example, polymerization of ethylene oxide onto 2-chloroethanol will produce a chloro-terminated polyol. This polyol can be reacted with an amine to produce a polyol with amine functionality on one terminus and a hydroxy group on the other.

The invention relates to: (Check as many as seem applicable):

☒ A composition of matter (compounds, alloy, plastic, mixture, etc.)

☒ A process (production, fabrication, use, treatment, etc.)

☐ A machine or article (tool, apparatus, package or other "thing")

2

List any literature (including patents) of which you are aware relating to the invention.

1. Croxall, W. J.; Dawson, N.D. US 3,021,341 (1962) [Miles Laboratories] describes the ethoxylation of 2-methyl-3-butyn-2-ol using ethylene oxide with $\text{BF}_3 \cdot \text{Et}_2\text{O}$ as the catalyst. The mono-ethoxylated compound was isolated by distillation for conversion to methylenedioxane by cyclization.
2. Petrow; Lagutschewa; ZOKHA4; Zh. Obshch. Khim.; 21; 1951; 1247, 1248, 1251; engl. Ausg.S. 1361, 1362, 1364 Ethoxylation of 2-methyl-3-butyn-2-ol with ethylene oxide using N,N-dimethylaniline at 150°C. [Under these conditions there was almost certainly some degradation of the alkynol occurring. Both mono- and diethoxylated products are prepared].

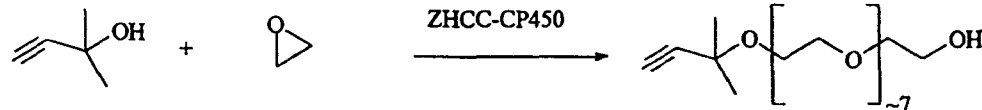
DESCRIPTION OF THE INVENTION

5

Set forth at least one working example demonstrating the invention in sufficient detail that others could repeat it and describe the preferred manner of practicing the invention. In your description, include--if applicable--performance data, chemical properties and analytical test results. If appropriate, use chemical formulas. Please include the range of proportions of the ingredients, temperature, time, pressure and other variables which you consider can be used in practicing the invention. In addition, state what equivalent materials might be useful in the invention. Use SI (metric) units in the description. If not otherwise apparent, state the invention's utility.

ZHCC-CP450, EO, and 2-Methyl-3-butyn-2-ol

4-20-99



g	265.51	~1050	6. = 4560 ppm
MW	84.12	44.05	
	d=.868	d=.882	
mol	3.156	23.83	
ratio	1	7.55	

2-methyl-3-butyn-2-ol : Air Products, dried over 3Å sieves
Catalyst used was Batch D prepared on p. 7

The catalyst was weighed into a 4 oz wide mouth bottle and dry 2-methyl-3-butyn-2-ol was weighed into a 500 mL narrow mouth bottle. The catalyst bottle was filled with a portion of the weighed amount of t-butynol and transferred into a reactor at B-4808 (Vicki Harrington). The catalyst bottle was then rinsed several times with t-butynol, transferring the washes into the reactor, followed by the remainder of the t-butynol. The reactor was then sealed and manually degassed/purged seven times with nitrogen (pressure not allowed to drop below atmospheric to prevent loss of initiator). The mixture was stirred and heated to 90°C. The EO line to the reactor was vented of nitrogen to fill the line with EO. A portion of EO (~50 g) was added and the mixture was heated and stirred while monitoring the pressure of the reactor to detect when the reaction had initiated. A small pressure drop was observed starting about 40 minutes after addition. A hour after the initial addition, an additional ~50 g of EO was added and the reactor pressure was watched. The pressure dropped more rapidly and the feed rate was put in automatic mode. This caused the feed rate to go above 10 g/min. As the reaction progressed a vigorous exotherm developed, reaching a differential of over 30°C from wall to reaction. This caused the system to become destabilized with wide swings in the jacket temperature causing wide swings in the reactor temperature from <80°C to more than 106°C for brief periods. The EO fed out rapidly and the reaction was digested quickly. The material was bottled out at ~20°C after stirring overnight in the reactor and was pale amber in color. The material was opaque, but remained liquid. Some settling was observed. NMR analysis clearly showed that the t-butynol had initiated the polymerization [shift of =C from 89 ppm to 85 ppm]. GPC analysis showed 380 Mn, PDI of 1.82.

Fractionation of Run 3 t-Butynol Polyol : 5-13-99

The polyol (Run 3 of t-butynol initiated [199900896-12]~1205 g) was slurried with 2410 g of isopropyl alcohol in a 6 L flask. The material was stirred and 1205 g of hexane was added. The mixture was stirred and chilled in an ice bath for several hours. The mixture was then vacuum filtered through a half inch pad of filter aid in a 3 L fritted glass funnel (coarse) The liquid stream was poured onto a paper filter to facilitate transfer without washing out the filter aid. The clear solution was concentrated by rotary evaporation to give a pale yellow liquid. The weight of the recovered low Mn polyol was 1078 g. The weight of the air dried wax was 109.09 g.

Catalyst preparation:

Potassium hexacyanocobaltate (8 g) dissolved in 140 mL of deionized water (HPLC grade) [Solution 1] was added to a commercial one speed blender (Waring model 33BL79). The blender was turned on and zinc chloride (25 g) dissolved in 40 mL of water [Solution 2] was added rapidly. A mixture of 100 mL of water and 100 mL of t-BuOH [Solution 3] was added immediately and the mixture was blended for 10 minutes (mixture became warm). The mixture was then rinsed into a 1 liter flask with Solution A [2 g CP-450 in 200 mL of water] and stirred for about 5 minutes, allowing the mixture to cool somewhat. The mixture was then vacuum filtered through 2 sheets of #1 Whatman paper (no product loss through filter), rinsing with about 20 mL of DI water. The wet cake was reblended with Solution B [2 g of CP-450 in 140 mL of water and 60 mL of t-BuOH] for 3 minutes in a centrifuge bottle and then centrifuged at 3000 rpm in the Mistral 3000E centrifuge for 25 minutes. The supernatant liquid was decanted and the mixture was reslurried in Solution C [1 g of CP-450 in 200 mL of t-BuOH] for several minutes and then centrifuged. The supernatant liquid was decanted and the solid was dried overnight at 75°C under vacuum (30 in.). The dried solids were ground in a mortar and pestle and transferred to a crystallizing dish for further drying to constant weight. Yield 12.00 g

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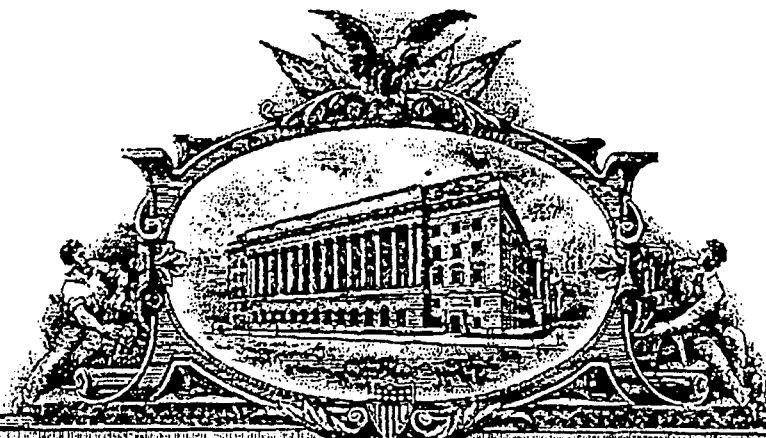
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***THIS IS TO CERTIFY that page (s) 481 is
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P. A. Hunt
Certifying Officer

AUG 14 2000
Date

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LOS ESTADOS UNIDOS DE AMERICA

A TODO AQUEL A QUIEN CONCIERNA LO PRESENTE

DEPARTAMENTO DE COMERCIO DE LOS ESTADOS UNIDOS

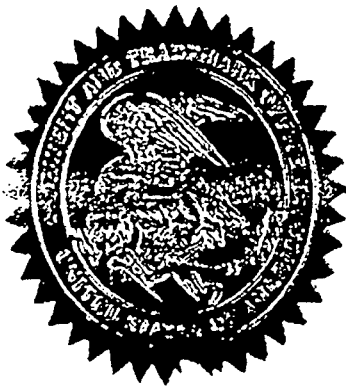
Oficina de Patentes y Marcas de los Estados Unidos

14 de agosto de 2000

LA PRESENTE ES PARA CERTIFICAR QUE ADJUNTA A LA MISMA HAY UNA COPIA FIEL DE LOS REGISTROS DE LA OFICINA DE PATENTES Y MARCAS DE LOS ESTADOS UNIDOS DE LOS DOCUMENTOS DE LA SOLICITUD DE PATENTE IDENTIFICADA EN LO QUE SIGUE, QUE CUMPLEN LOS REQUISITOS PARA OTORGARLE UNA FECHA DE PRESENTACIÓN BAJO 35 USC 111.

NÚMERO DE SOLICITUD: 60/143,079

FECHA DE PRESENTACIÓN: 09 de julio de 1999

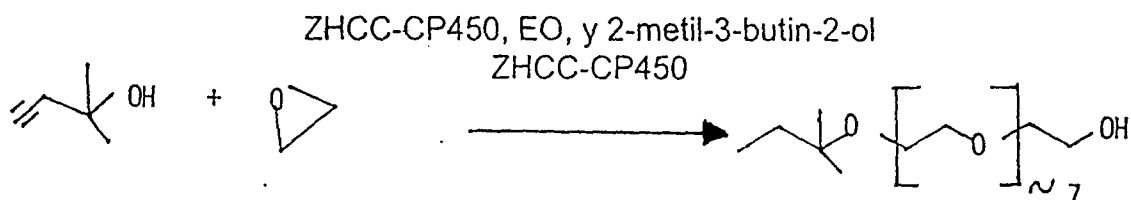


Por la Autoridad del
COMISARIO DE PATENTES Y MARCAS

P. R. GRANT
Oficial certificador

DESCRIPCIÓN DE LA INVENCION

Se establece por lo menos un ejemplo de trabajo que muestra la invención en suficiente detalle para que otros puedan repetirla y describe el modo preferido de la práctica de la invención. En la descripción debe incluir, si es aplicable, datos de comportamiento, propiedades químicas y resultados de análisis analíticos. Si es apropiado, use fórmulas químicas. Por favor incluya el rango de proporciones de los ingredientes, temperatura, tiempo, presión y otras variables que usted considere que pueden ser usadas al practicar la invención. Adicionalmente, establezca que materiales equivalentes pueden ser útiles en la invención. Use unidades SI (métricas) en la descripción. Si no es evidente, establezca la utilidad de la invención.



g	265,51	~1050	6. = 4560 ppm
MW	84,12	44,05	
d =	0,868	0,882	
mol	3,156	23,83	
proporción 1		7,55	

2-metil-3-butin-2-ol : Air Products, secado sobre tamices de 3Å
El catalizador usado fue la tanda D preparada en p. 7

El catalizador fue pesado en una botella de boca ancha de 4 oz. y el 2-metil-3-butin-2-ol seco fue pesado en una botella de boca angosta de 500 ml. La botella del catalizador se llenó con una porción de la cantidad pesada de t-butinol, y se transfirió al reactor en B-4808 (Vicki Harrington). La botella del catalizador fue entonces enjuagada varias veces con t-butinol, transfiriéndose los lavados al reactor, seguido por el resto del t-butinol. El reactor fue entonces sellado y se desgasificó/purgó siete veces manualmente con nitrógeno (no se permitió que la presión cayera por debajo de la atmosférica para impedir pérdida del iniciador). La mezcla fue agitada y calentada a 90°C. La línea EO al reactor se drenó del nitrógeno para llenar la línea con EO. Una porción de EO (~50g) se agregó y la mezcla fue calentada y agitada mientras se vigilaba la presión del reactor para detectar el momento de iniciación de la reacción. Una pequeña caída de presión fue observada iniciándose unos 40 minutos después de la adición. Una hora después de la adición inicial, se agregó adicionalmente ~50g de EO y se vigiló la presión del reactor. La presión cayó más rápidamente y la velocidad de alimentación se colocó en modo automático. Esto causó que la velocidad de alimentación pasara por encima de 10g/min. A medida que la reacción progresó un exotérmico vigoroso se desarrolló, alcanzando un diferencial de más de 30°C desde la pared a la reacción. Esto hizo que el sistema se desestabilizara con cambios amplios en la temperatura de la camisa causando vaivenes amplios en la temperatura del reactor desde <80°C a más de 106°C durante periodos breves. El EO se alimentó rápido y la reacción fue digerida rápidamente. El material fue embotellado a -20°C después de agitación durante la noche en el reactor y se obtuvo un color ambar pálido. El material era opaco, pero permaneció líquido. Algunos asentamientos fueron observados. El análisis NMR mostró claramente que

el t-butinol inició la polimerización [cambio de =C de 89 ppm a 85 ppm]. El análisis GPC mostró 380 Mn, PDI de 1,82.

Fraccionamiento de la corrida 3 de t-butinol poliol: 5-13-99

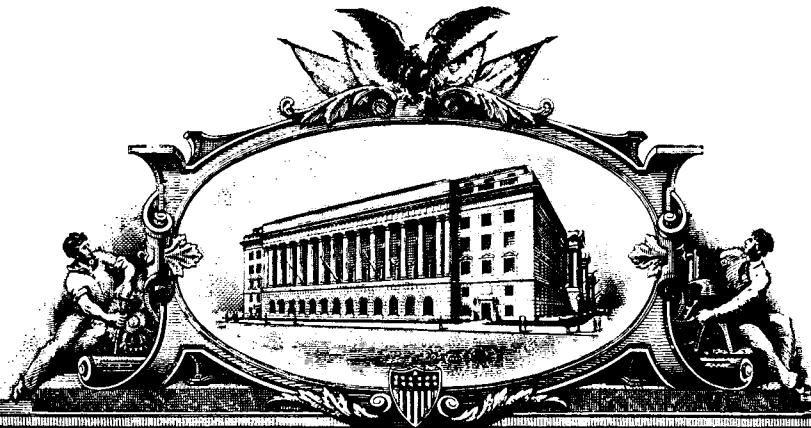
El poliol (corrida 3 de t-butinol se inició [199900896- 12] ~1205g) fue suspendido con 2410g de alcohol isopropilo en un frasco de 6 l. El material fue agitado y se agregaron 1205 g de hexano. La mezcla fue agitada y enfriada en un baño de hielo durante varias horas. La mezcla fue luego filtrada en vacío por una almohadilla de media pulgada de auxiliar de filtro en un embudo de vidrio frito (basto). La corriente de líquido fue vertida sobre filtro de papel para facilitar la transferencia sin lavar el auxiliar de filtro. La solución clara fue concentrada por evaporación giratoria para proporcionar un líquido amarillo pálido. El peso del poliol de bajo Mn recuperado fue de 1078 g. El peso de la cera secada al aire fue de 109,09 g.

Preparación del catalizador:

Hexacianocobaltato de potasio (8g) disuelto en 140 ml de agua desionizada (grado HPLC) [solución 1] fue agregado a un mezclador de una velocidad comercial (Waring Model 33BL79). Se energizó el mezclador y se agregó rápidamente cloruro de Cinc (25g) disuelto en 40 ml de agua [solución 2]. Se agregó una mezcla de 100 ml de agua y 100 ml de t-BuOH [solución 3] inmediatamente y la mezcla fue batida durante 10 minutos (la mezcla se calentó). La mezcla fue entonces enjuagada en un frasco de 1 litro con la solución A [2 g de CP-450 en 200 ml de agua] y se agitó durante cerca de 5 minutos, permitiendo que la mezcla se enfriara algo. Entonces la mezcla fue filtrada al vacío a través de 2 hojas de papel Whatman # 1 (no hubo pérdida de producto a través del filtro), enjuagando con cerca de 20 ml de agua DI. El ponqué húmedo se volvió a batir con la solución B [2 g de CP-450 en 140 ml de agua y 60 ml de t-BuOH] durante 3 minutos en una botella centrífuga y luego se centrifugo a 3000 rpm en la centrífuga Mistral 3000E durante 25 minutos. El líquido sobrenadante fue decantado y la mezcla fue resuspendida en la solución C [1 g de CP-450 en 200 ml de t-BuOH] durante varios minutos y luego se centrifugo. El líquido sobrenadante fue decantado y el sólido fue secado durante la noche a 75°C bajo vacío (30 Pulg.). Los sólidos secos fueron molidos en un mortero y triturador y se transfirió a un plato de cristalización para secado adicional hasta un peso constante. Producción 12,00 g.

COLO 00286-801-126-9

JBP/ld-1423



THE UNITED STATES OF AMERICA

TO ALL TO WHOM THESE PRESENTS SHALL COME:

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United States Patent and Trademark Office

August 11, 2000

THIS IS TO CERTIFY THAT ANNEXED HERETO IS A TRUE COPY FROM THE RECORDS OF THE UNITED STATES PATENT AND TRADEMARK OFFICE OF THOSE PAPERS OF THE BELOW IDENTIFIED PATENT APPLICATION THAT MET THE REQUIREMENTS TO BE GRANTED A FILING DATE UNDER 35 USC 111.

APPLICATION NUMBER: 60/143,081

FILING DATE: July 09, 1999



By Authority of the
COMMISSIONER OF PATENTS AND TRADEMARKS

P. SWAIN

Certifying Officer

Docket Number	60073	Type a plus sign (+) inside this box	+
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INVENTOR(s)/APPLICANT(s)			
LAST NAME	FIRST NAME	MIDDLE INITIAL	RESIDENCE (CITY AND EITHER STATE OR FOREIGN COUNTRY)
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Walker	Louis	L.	246 Barbara Drive, Clute, Texas 77531 United States of America
Wehmeyer	Richard	M.	205 Zinnia, Lake Jackson, Texas 77566 United States of America
Whitmarsh	Robert	H.	55 North Calla Lilly Ct, Lake Jackson, Texas 77566 United States of America

☐ Additional inventors are being named on separately numbered sheets attached hereto

TITLE OF THE INVENTION (280 characters max)
PROCESS FOR PREPARING POLYETHYLENE GLYCOLS FROM PRIMARY, SECONDARY, AND TERTIARY ALCOHOL INITIATORS USING A DOUBLE METAL CYANIDE CATALYST

CORRESPONDENCE ADDRESS	
Gene L. Tyler THE DOW CHEMICAL COMPANY Patent Department 2301 Brazosport Blvd. B-1211 Freeport, Texas 77541 U.S.A.	Telephone: 409-238-7239 Fax: 409-238-0878

ENCLOSED APPLICATION PARTS (check all that apply)	
☒ Specification	Number of Pages 4
☐ Drawing(s)	Number of Sheets
☐ Small Entity Statement	
☐ Other (specify)	

METHOD OF PAYMENT (check one)		
☐ A check or money order is enclosed to cover the Provisional filing fees	PROVISIONAL FILING FEE AMOUNT	\$150.00
☒ The Commissioner is hereby authorized to charge filing fees and credit Deposit Account Number: 04-1512		

The invention was made by an agency of the United States Government or under a contract with an agency of the United States Government

☒ No

☐ Yes, the name of the U.S. Government agency and the Government contract number are:

Respectfully submitted,

Gene L. Tyler
Registration No.: 35,395
Phone No.: 409-238-7239

EXPRESS MAIL MAILING NO.: EL026307204US
DATE OF DEPOSIT: July 9, 1999

GLT/II

PROVISIONAL APPLICATION FILING ONLY

DISCLOSURE OF INVENTION TO PATENT DEPARTMENT
THE DOW CHEMICAL COMPANY

00081
27

Approval of Department Head
Project No.:

Please fill out carefully. The requested information is needed for proper preparation of a patent application.

You are requested to use only the space provided to describe your invention and to attach additional pages only if necessary.

However, please attach any report which might prove beneficial in describing or understanding your invention. Call your Patent Department if you have a question.

DO NOT WRITE IN THIS SPACE	
Disclosure No.	60042
Assigned to	S
Date	

DOW
CONFIDENTIAL

TITLE OF INVENTION OR DISCOVERY: Process for Preparing Polyethylene glycols from Primary, Secondary and Tertiary Alcohol Initiators Using a Double Metal Cyanide Catalyst

Persons submitting this Disclosure of Invention:

I. Name (Please type or print):			
First	Katherine	Middle	S. Last Clement
Home Address	115 Poinciana		
City	Lake Jackson	County/Parish	Brazoria
State	Texas	Zip Code	77566
Citizenship	USA		
Occupation/Profession	Chemist		
Division	Texas	Bldg.	B-1215
Department	Materials Research & Synthesis	Lab Code	1260
Phone	409-297-2295	Master No.	144988

Signature			
I. Name (Please type or print)			
First	Richard	Middle	M. Last Wehmeyer
Home Address	205 Zinnia		
City	Lake Jackson	County/Parish	Brazoria
State	Texas	Zip Code	77566
Citizenship	USA		
Occupation/Profession	chemist		
Division	Texas	Bldg.	B-1215
Department	Materials Research & Synthesis	Lab Code	1260
Phone	409-238-9895	Master No.	093721

II. Name (Please type or print):			
First	Louis	Middle	L. Last Walker
Home Address	246 Barbara Drive		
City	Clute	County/Parish	Brazoria
State	Texas	Zip Code	77531
Citizenship	USA		
Occupation/Profession	Technologist		
Division	Texas	Bldg.	B-1215
Department	Materials Research & Synthesis	Lab Code	1260
Phone	409-238-9815	Master No.	139939

Signature			
IV. Name (Please type or print)			
First	Robert	Middle	H. Last Whitmarsh
Home Address	55 North Calla Lilly Ct.		
City	Lake Jackson	County/Parish	Brazoria
State	Texas	Zip Code	77566
Citizenship	USA		
Occupation/Profession	chemist		
Division	Texas	Bldg.	B-4810
Department	Polyglycols R&D	Lab Code	1054
Phone	409-238-4613	Master No.	143727

Was this invention made or completed in the course of work under a contract with any governmental agency or other outside party? YES NO

If YES, please identify the party and the contract

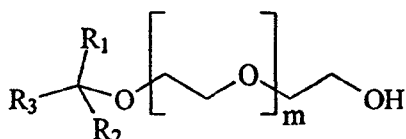
Witness:
I have read and understood this Disclosure and attachments.
My initials and date are included on all pages attached to this disclosure.

Type or print name of Witness	Signature	Date
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DESCRIPTION OF THE INVENTION

1

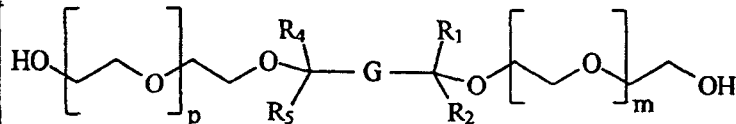
Give a summary/abstract of the Invention: Double metal cyanide catalysts have been used in the past to prepare polypropylene oxides from primary, secondary and tertiary alcohol initiators. However, the conventional wisdom from the teachings and the literature was that DMC catalysts could not be used to cap polypropylene glycols with ethylene oxide. It was an accepted fact that DMC complex catalysts would not polymerize ethylene oxide onto secondary or tertiary alcohols without forming large amounts of homopolymer (polyethyleneoxide diol). For example, in US patent 4,877,906 (Harper, S.D. to Arco Chemical Technology, Inc.) *Purification of Polyols prepared using Double Metal Cyanide Complex Catalysts* (1989) line 48 column 3 states "Direct ethylene oxide end-capping of propylene oxide polyols using double metal cyanide complex catalysis is not feasible due to the high reactivity of ethylene oxide and the consequent tendency to form highly ethoxylated by-products which are inhomogeneous with the remainder of the polyol." Also, due to the same fear of producing homopolymer, there do not appear to be any instances of using DMC catalysts to form ethoxylates of primary alcohols as well. Surprisingly, we have found that double metal cyanide catalysts will very efficiently polymerize ethylene oxide onto primary, secondary and tertiary alcohol initiators without forming large amounts of polyethylene diols.



The products correspond to the formula:

$R_1, R_2, R_3 = H$, or alkyl, optionally substituted with groups such as alkyne, alkene, $m > 1$

Other base sensitive groups such as ester, acid, halogen, etc. can be substituted onto the initiator. Other possible products correspond to the formula:



where $R_1, R_2, R_4, R_5 = H$, or alkyl; $G =$ alkyl, alkenyl, aryl, alkynyl, optionally substituted with groups such as ester, halo, etc.; $m, p > 1$

The reactions are carried out by adding the catalyst to the initiator in a stirred pressure vessel, adding up to 10% of the theoretical amount of ethylene oxide and heating the mixture at temperatures of 90-100°C until a decrease in pressure is observed, indicating that the reaction has initiated. The remaining ethylene oxide is then fed in at such a rate that the temperature is controlled at 90 to 100°C. Catalyst is used at levels from 30 ppm to 10,000 ppm.

The invention relates to: (Check as many as seem applicable):

☒ A composition of matter (compounds, alloy, plastic, mixture, etc.)

☒ A process (production, fabrication, use, treatment, etc.)

☐ A machine or article (tool, apparatus, package or other "thing")

2	List any literature (including patents) of which you are aware relating to the invention. 1. Jorgenson, M.W.; Budnik, R.; Miller, G.A. to Osi Specialties, Inc. US 5,856,369 Polyethers and Polysiloxane Copolymers Manufactured with Double Metal Cyanide Catalysts. Polyols are made by polymerizing a blend of PO and EO onto allyl alcohol or a tripropoxylate of allyl alcohol using DMC catalysts, specifically Zinc Hexacyanocobaltate catalyst. The examples specify that the catalyst (a glyme complex) must be activated with PO prior to the start of the PO and EO cofeed. 2. CRI 888124 Laycock, D.E.; Gobbi, G.C.; Sheehan, R.J. Zinc Hexacyanocobaltate Catalysis: Ethylene Oxide Capping of Homo-propylene Oxide Polyether Polyols. CP 700 and CP3000 were both reacted with EO at 125°C in the presence of Zinc Hexacyanocobaltate. (DEL 891 and 893) Conclusion made that EO would not react without forming polyethyleneoxide. 3. Petrow; Lagutschewa; ZOKHA4; Zh. Obshch. Khim.; 21; 1951; 1247, 1248, 1251; engl. Ausg.S. 1361, 1362, 1364 Ethoxylation of 2-methyl-3-butyn-2-ol with ethylene oxide using N,N-dimethylaniline at 150°C. [Under these conditions there was almost certainly some degradation of the alkynol occurring. Both mono- and diethoxylated products are prepared]. 4. Herold, R.J.; Bingham, R.E., Brevet D'Invention No. 81 18520 General Tire and Rubber, Co., (1981) on preferred method for removal of ZHCC catalyst residues from homo-PO polyol, also recommends this procedure as a means of capping the homo-PO polyol with EO, implying that ZHCC causes EO to homopolymerize. 5. Harper, S.D. to Arco Chemical Technology, Inc., US 4,877,906 Purification of Polyols prepared using Double Metal Cyanide Complex Catalysts (1989) line 48 column 3 "Direct ethylene oxide end-capping of propylene oxide polyols using double metal cyanide complex catalysis is not feasible due to the high reactivity of ethylene oxide and the consequent tendency to form highly ethoxylated by-products which are inhomogeneous with the remainder of the polyol." 6. Numerous other Arco and General Tire patents also teach that EO cannot be polymerized onto the secondary hydroxyl groups of PO polyols with double metal cyanide complex catalysis due to the formation of large amounts of polyethylene oxide. 7. CRI 1339 Bergeron, S., Badhwar, A.; Facca, M.; Laycock, D.E.; Rudolf, P. Review and Evaluation of Competitive Technology for Synthesis and Use of DMC Catalysts and Recent Modifications by Dow. (Aug. 1998) and references contained within.
3	State the nature and extent of your literature search. Scifinder search of "alkyne functionalized polyols or acetylene containing polyethylene glycols or polypropylene glycols" and "double metal cyanide" Beilstein search of ethoxylate structure of 2-methyl-3-butyn-2-ol. Derwent search of polyethylene glycol of 2-methyl-3-buten-2-ol.
4	How does this invention differ from, and list its advantages over, the literature known to you as well as the alternatives, if any, currently being employed. : Use of DMC catalysts to react EO onto secondary and tertiary alcohol groups has not been reported in the literature. We have also not found reference to DMC having been used as the catalyst to ethoxylate primary alcohol initiators. The polyethers prepared from tertiary alcohols using DMC have narrower polydispersities than the polyethers prepared from tertiary alcohol initiators using KOH as the catalyst. For example, even a low molecular weight polyethylene glycol (500 MW) product prepared from 2-methyl-3-buten-2-ol was a solid at room temperature. Acid catalysis of oxide polymerizations onto tertiary alcohols also produce products having broad polydispersities. In addition, under acid catalysis cyclic by-products are also a problem. Also, under acid catalysis, tertiary alcohols can form stable carbonium ions which can produce an additional type of byproduct by reacting with the hydroxy end-groups of the polyol, thus "capping" the chain. In the present invention using double metal cyanide catalysts, the polyethers produced using tertiary alcohol initiators exhibit narrow polydispersity. No "capped" products are produced. Only a trace quantity of any other by-products are seen. The molecular weight distribution is bimodal, with the major portion exhibiting the desired molecular weight target with a polydispersity typically of less than 1.6. A small amount of high molecular weight by-product is produced, also having a narrow polydispersity. Because of the narrow polydispersity, and the low level of high molecular weight fraction, the low molecular weight products remain liquid at room temperature. In the case of polyethylene glycols with DP of < 12, the minor high molecular weight component crystallizes from the mixture and can be separated using a solvent fractionation. Examples of alcohols useful as initiators include 2-methyl-3-butyn-2-ol; 2-methyl-3-buten-2-ol; t-butanol; 2,5-dimethyl-3-hexyn-2,5-diol, 2,4,7,9-tetramethyl-5-decyne-4,7-diol, and the like. The catalyst also allows the presence of functional groups sensitive to base, such as halo, alkyne, ester, etc.

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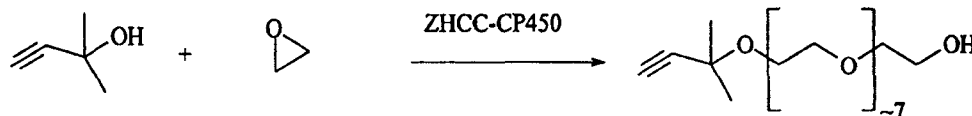
DESCRIPTION OF THE INVENTION

00084

5

Set forth at least one working example demonstrating the invention in sufficient detail that others could repeat it and describe the preferred manner of practicing the invention. In your description, include--if applicable--performance data, chemical properties and analytical test results. If appropriate, use chemical formulas. Please include the range of proportions of the ingredients, temperature, time, pressure and other variables which you consider can be used in practicing the invention. In addition, state what equivalent materials might be useful in the invention. Use SI (metric) units in the description. If not otherwise apparent, state the invention's utility.

ZHCC-CP450, EO, and 2-Methyl-3-butyn-2-ol 4-20-99



g	265.51	~1050	6. = 4560 ppm
MW	84.12	44.05	
	d=.868	d=.882	
mol	3.156	23.83	
ratio	1	7.55	

2-methyl-3-butyn-2-ol : Air Products, dried over 3Å sieves
Catalyst used was Batch D prepared on p. 7

The catalyst was weighed into a 4 oz wide mouth bottle and dry 2-methyl-3-butyn-2-ol was weighed into a 500 mL narrow mouth bottle. The catalyst bottle was filled with a portion of the weighed amount of t-butynol and transferred into a reactor at B-4808 (Vicki Harrington). The catalyst bottle was then rinsed several times with t-butynol, transferring the washes into the reactor, followed by the remainder of the t-butynol. The reactor was then sealed and manually degassed/purged seven times with nitrogen (pressure not allowed to drop below atmospheric to prevent loss of initiator). The mixture was stirred and heated to 90°C. The EO line to the reactor was vented of nitrogen to fill the line with EO. A portion of EO (~50 g) was added and the mixture was heated and stirred while monitoring the pressure of the reactor to detect when the reaction had initiated. A small pressure drop was observed starting about 40 minutes after addition. A hour after the initial addition, an additional ~50 g of EO was added and the reactor pressure was watched. The pressure dropped more rapidly and the feed rate was put in automatic mode. This caused the feed rate to go above 10 g/min. As the reaction progressed a vigorous exotherm developed, reaching a differential of over 30°C from wall to reaction. This caused the system to become destabilized with wide swings in the jacket temperature causing wide swings in the reactor temperature from <80°C to more than 106°C for brief periods. The EO fed out rapidly and the reaction was digested quickly. The material was bottled out at ~20°C after stirring overnight in the reactor and was pale amber in color. The material was opaque, but remained liquid. Some settling was observed. NMR analysis clearly showed that the t-butynol had initiated the polymerization [shift of =C from 89 ppm to 85 ppm]. GPC analysis showed 380 Mn, PDI of 1.82.

Fractionation of Run 3 t-Butynol Polyol : 5-13-99

The polyol (Run 3 of t-butynol initiated [199900896-12]~1205 g) was slurried with 2410 g of isopropyl alcohol in a 6 L flask. The material was stirred and 1205 g of hexane was added. The mixture was stirred and chilled in an ice bath for several hours. The mixture was then vacuum filtered through a half inch pad of filter aid in a 3 L fritted glass funnel (coarse) The liquid stream was poured onto a paper filter to facilitate transfer without washing out the filter aid. The clear solution was concentrated by rotary evaporation to give a pale yellow liquid. The weight of the recovered low Mn polyol was 1078 g. The weight of the air dried wax was 109.09 g.

Catalyst preparation:

Potassium hexacyanocobaltate (8 g) dissolved in 140 mL of deionized water (HPLC grade) [Solution 1] was added to a commercial one speed blender (Waring model 33BL79). The blender was turned on and zinc chloride (25 g) dissolved in 40 mL of water [Solution 2] was added rapidly. A mixture of 100 mL of water and 100 mL of t-BuOH [Solution 3] was added immediately and the mixture was blended for 10 minutes (mixture became warm). The mixture was then rinsed into a 1 liter flask with Solution A [2 g CP-450 in 200 mL of water] and stirred for about 5 minutes, allowing the mixture to cool somewhat. The mixture was then vacuum filtered through 2 sheets of #1 Whatman paper (no product loss through filter), rinsing with about 20 mL of DI water. The wet cake was reblended with Solution B [2 g of CP-450 in 140 mL of water and 60 mL of t-BuOH] for 3 minutes in a centrifuge bottle and then centrifuged at 3000 rpm in the Mistral 3000E centrifuge for 25 minutes. The supernatant liquid was decanted and the mixture was reslurried in Solution C [1 g of CP-450 in 200 mL of t-BuOH] for several minutes and then centrifuged. The supernatant liquid was decanted and the solid was dried overnight at 75°C under vacuum (30 in.). The dried solids were ground in a mortar and pestle and transferred to a crystallizing dish for further drying to constant weight. Yield 12.00 g



LOS ESTADOS UNIDOS DE AMÉRICA

A TODO AQUEL A QUIEN CONCIERNA LO PRESENTE

DEPARTAMENTO DE COMERCIO DE LOS ESTADOS UNIDOS

Oficina de Patentes y Marcas de los Estados Unidos

11 de agosto de 2000

LA PRESENTE ES PARA CERTIFICAR QUE ADJUNTA A LA MISMA HAY UNA COPIA FIEL DE LOS REGISTROS DE LA OFICINA DE PATENTES Y MARCAS DE LOS ESTADOS UNIDOS DE LOS DOCUMENTOS DE LA SOLICITUD DE PATENTE IDENTIFICADA EN LO QUE SIGUE, QUE CUMPLEN LOS REQUISITOS PARA OTORGARLE UNA FECHA DE PRESENTACIÓN BAJO 35 USC 111.

NÚMERO DE SOLICITUD: 60/143,081

FECHA DE PRESENTACIÓN: 09 de julio de 1999

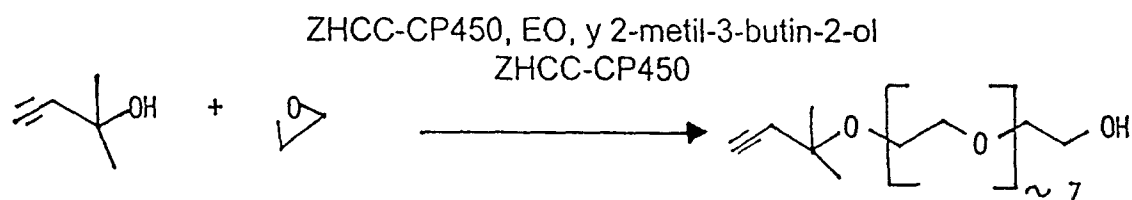


Por la Autoridad del
COMISARIO DE PATENTES Y MARCAS

P. SWAIN
Oficial certificador

DESCRIPCIÓN DE LA INVENCION

Se establece por lo menos un ejemplo de trabajo que muestra la invención en suficiente detalle para que otros puedan repetirla y describe el modo preferido de la práctica de la invención. En la descripción debe incluir, si es aplicable, datos de comportamiento, propiedades químicas y resultados de análisis analíticos. Si es apropiado, use fórmulas químicas. Por favor incluya el rango de proporciones de los ingredientes, temperatura, tiempo, presión y otras variables que usted considere que pueden ser usadas al practicar la invención. Adicionalmente, establezca que materiales equivalentes pueden ser útiles en la invención. Use unidades SI (métricas) en la descripción. Si no es evidente, establezca la utilidad de la invención.



g	265,51	~1050	6. = 4560 ppm
MW	84,12	44,05	
d =	0,868	0,882	
mol	3,156	23,83	
proporción 1		7,55	

2-metil-3-butin-2-ol : Air Products, secado sobre tamices de 3Å
El catalizador usado fue la tanda D preparada en p. 7

El catalizador fue pesado en una botella de boca ancha de 4 oz. y el 2-metil-3-butin-2-ol seco fue pesado en una botella de boca angosta de 500 ml. La botella del catalizador se llenó con una porción de la cantidad pesada de t-butinol, y se transfirió al reactor en B-4808 (Vicki Harrington). La botella del catalizador fue entonces enjuagada varias veces con t-butinol, transfiriéndose los lavados al reactor, seguido por el resto del t-butinol. El reactor fue entonces sellado y se desgasificó/purgó siete veces manualmente con nitrógeno (no se permitió que la presión cayera por debajo de la atmosférica para impedir pérdida del iniciador). La mezcla fue agitada y calentada a 90°C. La línea EO al reactor se drenó del nitrógeno para llenar la línea con EO. Una porción de EO (~50g) se agregó y la mezcla fue calentada y agitada mientras se vigilaba la presión del reactor para detectar el momento de iniciación de la reacción. Una pequeña caída de presión fue observada iniciándose unos 40 minutos después de la adición. Una hora después de la adición inicial, se agregó adicionalmente ~50g de EO y se vigiló la presión del reactor. La presión cayó más rápidamente y la velocidad de alimentación se colocó en modo automático. Esto causó que la velocidad de alimentación pasara por encima de 10g/min. A medida que la reacción progresó un exotérmico vigoroso se desarrolló, alcanzando un diferencial de más de 30°C desde la pared a la reacción. Esto hizo que el sistema se desestabilizara con cambios amplios en la temperatura de la camisa causando vaivenes amplios en la temperatura del reactor desde <80°C a más de 106°C durante periodos breves. El EO se alimentó rápido y la reacción fue digerida rápidamente. El material fue embotellado a -20°C después de agitación durante la noche en el reactor y se obtuvo un color ámbar pálido. El material era opaco, pero permaneció líquido. Algunos asentamientos fueron observados. El análisis NMR mostró claramente que el t-butinol inició la polimerización [cambio de =C de 89 ppm a 85 ppm]. El análisis GPC mostró 380 Mn, PDI de 1,82. Fraccionamiento de la corrida 3 de t-butinol polioli: 5-13-99

El poliol (corrida 3 de t-butinol se inició [199900896- 12] ~1205g) fue suspendido con 2410g de alcohol isopropilo en un frasco de 6 l. El material fue agitado y se agregaron 1205 g de hexano. La mezcla fue agitada y enfriada en un baño de hielo durante varias horas. La mezcla fue luego filtrada en vacío por una almohadilla de media pulgada de auxiliar de filtro en un embudo de vidrio frito (basto). La corriente de líquido fue vertida sobre filtro de papel para facilitar la transferencia sin lavar el auxiliar de filtro. La solución clara fue concentrada por evaporación giratoria para proporcionar un líquido amarillo pálido. El peso del poliol de bajo Mn recuperado fue de 1078 g. El peso de la cera secada al aire fue de 109,09 g.

Preparación del catalizador:

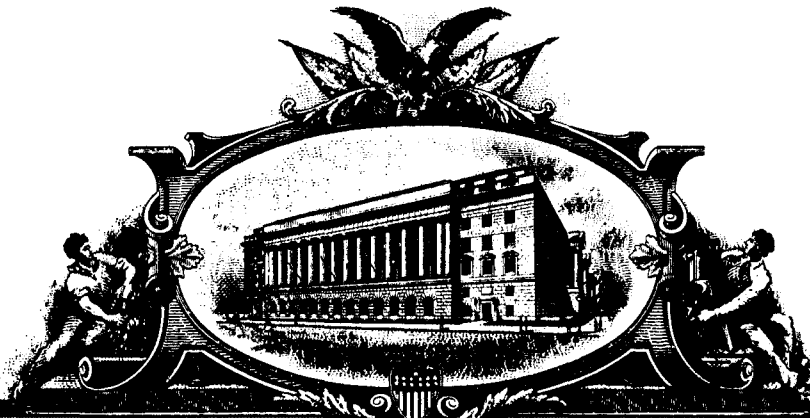
Hexacianocobaltato de potasio (8g) disuelto en 140 ml de agua desionizada (grado HPLC) [solución 1] fue agregado a un mezclador de una velocidad comercial (Waring Model 33BL79). Se energizó el mezclador y se agregó rápidamente cloruro de Cinc (25g) disuelto en 40 ml de agua [solución 2]. Se agregó una mezcla de 100 ml de agua y 100 ml de t-BuOH [solución 3] inmediatamente y la mezcla fue batida durante 10 minutos (la mezcla se calentó). La mezcla fue entonces enjuagada en un frasco de 1 litro con la solución A [2 g de CP-450 en 200 ml de agua] y se agitó durante cerca de 5 minutos, permitiendo que la mezcla se enfriara algo. Entonces la mezcla fue filtrada al vacío a través de 2 hojas de papel Whatman # 1 (no hubo pérdida de producto a través del filtro), enjuagando con cerca de 20 ml de agua DI. El ponqué húmedo se volvió a batir con la solución B [2 g de CP-450 en 140 ml de agua y 60 ml de t-BuOH] durante 3 minutos en una botella centrífuga y luego se centrífugo a 3000 rpm en la centrífuga Mistral 3000E durante 25 minutos. El líquido sobrenadante fue decantado y la mezcla fue resuspendida en la solución C [1 g de CP-450 en 200 ml de t-BuOH] durante varios minutos y luego se centrífugo. El líquido sobrenadante fue decantado y el sólido fue secado durante la noche a 75°C bajo vacío (30 Pulg.). Los sólidos secos fueron molidos en un mortero y triturador y se transfirió a un plato de cristalización para secado adicional hasta un peso constante. Producción 12,00 g.

COLO 00286-801-126-9

JBP/lld-1428

00039 84

PA 289135



THE UNITED STATES OF AMERICA

TO ALL TO WHOM THESE PRESENTS SHALL COME:

UNITED STATES DEPARTMENT OF COMMERCE

United States Patent and Trademark Office

August 14, 2000

THIS IS TO CERTIFY THAT ANNEXED HERETO IS A TRUE COPY FROM THE RECORDS OF THE UNITED STATES PATENT AND TRADEMARK OFFICE OF THOSE PAPERS OF THE BELOW IDENTIFIED PATENT APPLICATION THAT MET THE REQUIREMENTS TO BE GRANTED A FILING DATE UNDER 35 USC 111.

APPLICATION NUMBER: 60/143,082

FILING DATE: July 09, 1999



**By Authority of the
COMMISSIONER OF PATENTS AND TRADEMARKS**

H. L. Jackson

H. L. JACKSON

Certifying Officer

3553 U.S. PTO
07/00/00

Approval for use through OMB 0651-00XX
Patent and Trademark Office, U S DEPARTMENT OF COMMERCE

PTO XXXX
35

PROVISIONAL APPLICATION COVER SHEET

0009

request for filing a PROVISIONAL APPLICATION under 35 CFR 1.53 (c).

Docket Number	60070	Type a plus sign (+) inside this box	+
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INVENTOR(s)/APPLICANT(s)

LAST NAME	FIRST NAME	MIDDLE INITIAL	RESIDENCE (CITY AND EITHER STATE OR FOREIGN COUNTRY)
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Whitmarsh	Robert	H.	55 North Calla Lilly Ct, Lake Jackson, Texas 77566 United States of America

☐ Additional inventors are being named on separately numbered sheets attached hereto

TITLE OF THE INVENTION (280 characters max)

PROCESS FOR PREPARING NARROW POLYDISPERSITY POLYOXIDES FROM TERTIARY INITIATORS

CORRESPONDENCE ADDRESS

Gene L. Tyler
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Patent Department
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Fax: 409-238-0878

ENCLOSED APPLICATION PARTS (check all that apply)

- ☒ Specification Number of Pages 4 ☐ Small Entity Statement
☐ Drawing(s) Number of Sheets _____ ☐ Other (specify)

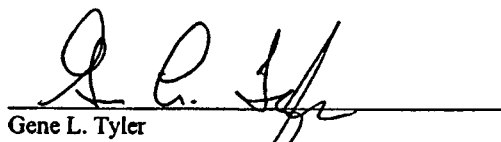
METHOD OF PAYMENT (check one)

☐ A check or money order is enclosed to cover the Provisional filing fees	PROVISIONAL FILING FEE AMOUNT	\$150.00
☒ The Commissioner is hereby authorized to charge filing fees and credit Deposit Account Number: 04-1512		

The invention was made by an agency of the United States Government or under a contract with an agency of the United States Government

- ☒ No
☐ Yes, the name of the U.S. Government agency and the Government contract number are:

Respectfully submitted,


Gene L. Tyler
Registration No.: 35,395
Phone No.: 409-238-7239

EXPRESS MAIL MAILING NO.: EL026307204US
DATE OF DEPOSIT: July 9, 1999

GLT/II

PROVISIONAL APPLICATION FILING ONLY

DISCLOSURE OF INVENTION TO PATENT DEPARTMENT
THE DOW CHEMICAL COMPANY

00091

Approval of Department Head _____
Object No.: _____

Please fill out carefully. The requested information is needed for proper preparation of a patent application.
You are requested to use only the space provided to describe your invention and to attach additional pages only if necessary.
However, please attach any report which might prove beneficial in describing or understanding your invention. Call your Patent Department if you have a question.

DO NOT WRITE IN THIS SPACE
Disclosure No. 60070
Assigned to: _____ Date: _____

DOW
CONFIDENTIAL

TITLE OF INVENTION OR DISCOVERY: Process for Preparing Narrow Polydispersity Polyoxides from tertiary initiators

I. Persons submitting this Disclosure of Invention:

Name (Please type or print):
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Citizenship USA
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Citizenship USA
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Division Texas Bldg. B-4810
Department Polyglycols R&D Lab
Code 1054
Phone 409-238-4613 Master No. 143727

Signature _____

Was this invention made or completed in the course of work under a contract with any governmental agency or other outside party?
If YES, please identify the party and the contract

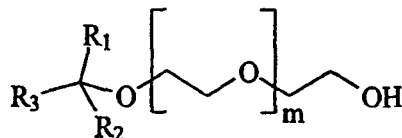
Witness:
I have read and understood this Disclosure and attachments.
My initials and date are included on all pages attached to this disclosure.

Type or print name of Witness _____ Signature _____ Date _____

DESCRIPTION OF THE INVENTION

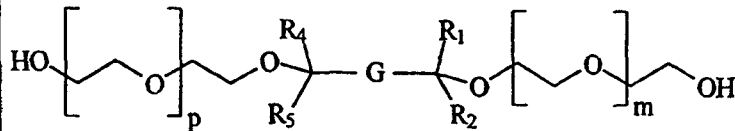
1

Give a summary/abstract of the Invention: Polyoxides prepared from tertiary alcohol initiators using KOH or NaOH as the catalyst typically exhibit broad polydispersities. For example, using standard base catalysis even a low target molecular weight polyethylene glycol (500 MW) product prepared from 2-methyl-3-buten-2-ol is a solid at room temperature. Product produced from primary alcohols with a target molecular weight of 500 using standard base catalysis are liquids at room temperature. In the present invention using double metal cyanide catalysts, the polyoxides produced using tertiary alcohol initiators exhibit narrow polydispersity. The molecular weight distribution is bimodal, with the major portion exhibiting the desired molecular weight target with a polydispersity of less than 1.5. A small amount of high molecular weight by-product is produced, also having a narrow polydispersity. Because of the narrow polydispersity, the low molecular weight products remain liquid at room temperature. In the case of polyethylene glycols, the minor high molecular weight component crystallizes from the mixture and can be separated using a solvent fractionation. Examples of alcohols useful as initiators include 2-methyl-3-buten-2-ol; 2-methyl-3-buten-2-ol; t-butanol; 2,5-dimethyl-3-hexyn-2,5-diol, 2,4,7,9-tetramethyl-5-decyne-4,7-diol, and the like.



The products correspond to the formula:

$R_1, R_2, R_3 = H$, or alkyl, optionally substituted with groups such as ester, halo, etc.; $m > 1$ and the formula:



where $R_1, R_2, R_4, R_5 = H$, or alkyl; $G =$ alkyl, alkenyl, aryl, alkynyl, optionally substituted with groups such as ester, halo, etc.; $m, p > 1$

The reactions are carried out by adding the catalyst to the initiator in a stirred pressure vessel, adding up to 10% of the theoretical amount of oxide and heating the mixture at temperatures of 90-100°C until a decrease in pressure is observed, indicating that the reaction has initiated. The remaining oxide is then fed in at such a rate that the temperature is controlled at 90 to 100°C. Catalyst is used at levels from 30 ppm to 10,000 ppm.

The invention relates to: (Check as many as seem applicable):

☐ A composition of matter (compounds, alloy, plastic, mixture, etc.)

☒ A process (production, fabrication, use, treatment, etc.)

☐ A machine or article (tool, apparatus, package or other "thing")

2

- List any literature (including patents) of which you are aware relating to the invention. 1. Croxall, W. J.; Dawson, N.D. US 3,021,341 (1962) [Miles Laboratories] describes the ethoxylation of 2-methyl-3-buten-2-ol using ethylene oxide with $BF_3 \cdot Et_2O$ as the catalyst. The mono-ethoxylated compound was isolated by distillation for conversion to methylenedioxane by cyclization.
2. Petrow; Lagutschewa; ZOKHA4; Zh. Obshch. Khim.; 21; 1951; 1247, 1248, 1251; engl. Ausg.S. 1361, 1362, 1364 Ethoxylation of 2-methyl-3-buten-2-ol with ethylene oxide using N,N-dimethylaniline at 150°C. [Under these conditions there was almost certainly some degradation of the alkynol occurring. Both mono- and diethoxylated products are prepared].
- 3.

3

State the nature and extent of your literature search. Scifinder search of "alkyne functionalized polyols or acetylene containing polyethylene glycols or polypropylene glycols" Beilstein search of ethoxylate structure of 2-methyl-3-buten-2-ol. Derwent search of polyethylene glycol of 2-methyl-3-buten-2-ol.

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4	How does this invention differ from, and list its advantages over, the literature known to you as well as the alternatives, if any, currently being employed. : Polyethers prepared from tertiary alcohol initiators using KOH as the catalyst typically exhibit broad polydispersities. Polydispersity can be an important variable in a number of end-uses. In the specific case of ethoxylates with a targeted degree of polymerization of 6 to 12 EO units, products made using KOH have a broad polydispersity resulting in a solid product at room temperature. Acid catalysis of oxide polymerizations onto tertiary alcohols also produce products having broad polydispersities. In addition, under acid catalysis cyclic by-products are also a problem. Also, under acid catalysis, tertiary alcohols can form stable carbonium ions which can produce an additional type of by-product by reacting with the hydroxy end-groups of the polyol, thus "capping" the chain. In the present invention using double metal cyanide catalysts, the polyethers produced using tertiary alcohol initiators exhibit narrow polydispersity. No "capped" products are produced. Only trace quantities of any other by-products are seen. The molecular weight distribution is bimodal, with the major portion exhibiting the desired molecular weight target with a polydispersity typically of less than 1.6. A small amount of high molecular weight by-product is produced, also having a narrow polydispersity. Again, in the specific case of ethoxylates with a targeted degree of polymerization of 6 to 12 EO units, the minor high molecular weight component crystallizes from the mixture and can be separated using a solvent fractionation. Examples of alcohols useful as initiators include 2-methyl-3-butyn-2-ol; 2-methyl-3-buten-2-ol; t-butanol; 2,5-dimethyl-3-hexyn-2,5-diol, 2,4,7,9-tetramethyl-5-decyne-4,7-diol, and the like. The catalyst also allows the presence of functional groups sensitive to base, such as halo, alkyne, ester, etc.

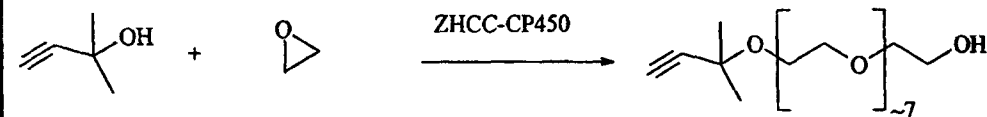
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DESCRIPTION OF THE INVENTION

5

Set forth at least one working example demonstrating the invention in sufficient detail that others could repeat it and describe the preferred manner of practicing the invention. In your description, include--if applicable--performance data, chemical properties and analytical test results. If appropriate, use chemical formulas. Please include the range of proportions of the ingredients, temperature, time, pressure and other variables which you consider can be used in practicing the invention. In addition, state what equivalent materials might be useful in the invention. Use SI (metric) units in the description. If not otherwise apparent, state the invention's utility.

ZHCC-CP450, EO, and 2-Methyl-3-butyn-2-ol 4-20-99



g	265.51	~1050	6. = 4560 ppm
MW	84.12	44.05	
	d=.868	d=.882	
mol	3.156	23.83	
ratio	1	7.55	

2-methyl-3-butyn-2-ol : Air Products, dried over 3Å sieves
Catalyst used was Batch D prepared on p. 7

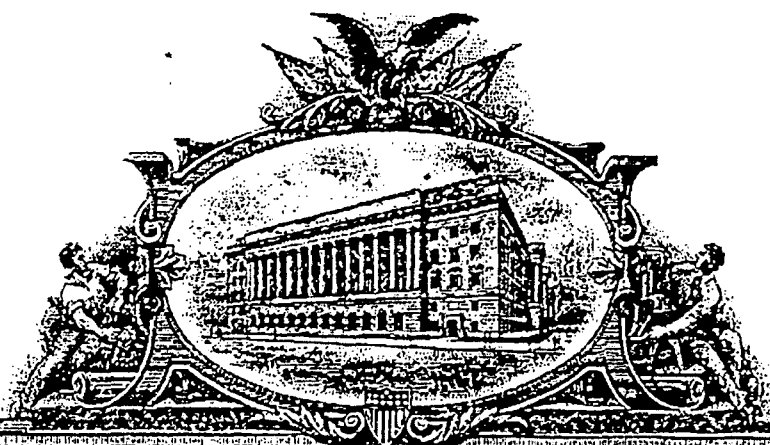
The catalyst was weighed into a 4 oz wide mouth bottle and dry 2-methyl-3-butyn-2-ol was weighed into a 500 mL narrow mouth bottle. The catalyst bottle was filled with a portion of the weighed amount of t-butynol and transferred into a reactor at B-4808 (Vicki Harrington). The catalyst bottle was then rinsed several times with t-butynol, transferring the washes into the reactor, followed by the remainder of the t-butynol. The reactor was then sealed and manually degassed/purged seven times with nitrogen (pressure not allowed to drop below atmospheric to prevent loss of initiator). The mixture was stirred and heated to 90°C. The EO line to the reactor was vented of nitrogen to fill the line with EO. A portion of EO (~50 g) was added and the mixture was heated and stirred while monitoring the pressure of the reactor to detect when the reaction had initiated. A small pressure drop was observed starting about 40 minutes after addition. A hour after the initial addition, an additional ~50 g of EO was added and the reactor pressure was watched. The pressure dropped more rapidly and the feed rate was put in automatic mode. This caused the feed rate to go above 10 g/min. As the reaction progressed a vigorous exotherm developed, reaching a differential of over 30°C from wall to reaction. This caused the system to become destabilized with wide swings in the jacket temperature causing wide swings in the reactor temperature from <80°C to more than 106°C for brief periods. The EO fed out rapidly and the reaction was digested quickly. The material was bottled out at ~20°C after stirring overnight in the reactor and was pale amber in color. The material was opaque, but remained liquid. Some settling was observed. NMR analysis clearly showed that the t-butynol had initiated the polymerization [shift of =C from 89 ppm to 85 ppm]. GPC analysis showed 380 Mn, PDI of 1.82.

Fractionation of Run 3 t-Butynol Polyol : 5-13-99

The polyol (Run 3 of t-butynol initiated [199900896-12]~1205 g) was slurried with 2410 g of isopropyl alcohol in a 6 L flask. The material was stirred and 1205 g of hexane was added. The mixture was stirred and chilled in an ice bath for several hours. The mixture was then vacuum filtered through a half inch pad of filter aid in a 3 L fritted glass funnel (coarse) The liquid stream was poured onto a paper filter to facilitate transfer without washing out the filter aid. The clear solution was concentrated by rotary evaporation to give a pale yellow liquid. The weight of the recovered low Mn polyol was 1078 g. The weight of the air dried wax was 109.09 g.

Catalyst preparation:

Potassium hexacyanocobaltate (8 g) dissolved in 140 mL of deionized water (HPLC grade) [Solution 1] was added to a commercial one speed blender (Waring model 33BL79). The blender was turned on and zinc chloride (25 g) dissolved in 40 mL of water [Solution 2] was added rapidly. A mixture of 100 mL of water and 100 mL of t-BuOH [Solution 3] was added immediately and the mixture was blended for 10 minutes (mixture became warm). The mixture was then rinsed into a 1 liter flask with Solution A [2 g CP-450 in 200 mL of water] and stirred for about 5 minutes, allowing the mixture to cool somewhat. The mixture was then vacuum filtered through 2 sheets of #1 Whatman paper (no product loss through filter), rinsing with about 20 mL of DI water. The wet cak was reblended with Solution B [2 g of CP-450 in 140 mL of water and 60 mL of t-BuOH] for 3 minutes in a centrifuge bottle and then centrifuged at 3000 rpm in the Mistral 3000E centrifuge for 25 minutes. The supernatant liquid was decanted and the mixture was reslurried in Solution C [1 g of CP-450 in 200 mL of t-BuOH] for several minutes and then centrifuged. The supernatant liquid was decanted and the solid was dried overnight at 75°C under vacuum (30 in.). The dried solids were ground in a mortar and pestle and transferred to a crystallizing dish for further drying to constant weight. Yield 12.00 g



LOS ESTADOS UNIDOS DE AMERICA

A TODO AQUEL A QUIEN CONCIERNA LO PRESENTE

DEPARTAMENTO DE COMERCIO DE LOS ESTADOS UNIDOS

Oficina de Patentes y Marcas de los Estados Unidos

14 de agosto de 2000

LA PRESENTE ES PARA CERTIFICAR QUE ADJUNTA A LA MISMA HAY UNA COPIA FIEL DE LOS REGISTROS DE LA OFICINA DE PATENTES Y MARCAS DE LOS ESTADOS UNIDOS DE LOS DOCUMENTOS DE LA SOLICITUD DE PATENTE IDENTIFICADA EN LO QUE SIGUE, QUE CUMPLEN LOS REQUISITOS PARA OTORGARLE UNA FECHA DE PRESENTACIÓN BAJO 35 USC 111.

NÚMERO DE SOLICITUD: 60/143,082

FECHA DE PRESENTACIÓN: 09 de julio de 1999

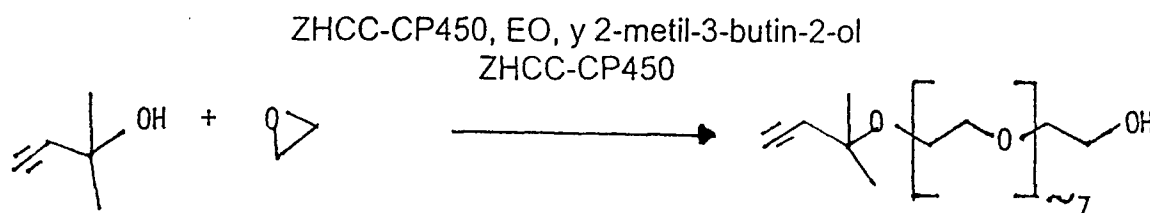


Por la Autoridad del
COMISARIO DE PATENTES Y MARCAS

H.L. JACKSON
Oficial certificador

DESCRIPCIÓN DE LA INVENCIÓN

Se establece por lo menos un ejemplo de trabajo que muestra la invención en suficiente detalle para que otros puedan repetirla y describe el modo preferido de la práctica de la invención. En la descripción debe incluir, si es aplicable, datos de comportamiento, propiedades químicas y resultados de análisis analíticos. Si es apropiado, use fórmulas químicas. Por favor incluya el rango de proporciones de los ingredientes, temperatura, tiempo, presión y otras variables que usted considere que pueden ser usadas al practicar la invención. Adicionalmente, establezca que materiales equivalentes pueden ser útiles en la invención. Use unidades SI (métricas) en la descripción. Si no es evidente, establezca la utilidad de la invención.



g	265,51	~1050	6. = 4560 ppm
MW	84,12	44,05	
d =	0,868	0,882	
mol	3,156	23,83	
proporción 1		7,55	

2-metil-3-butin-2-ol : Air Products, secado sobre tamices de 3Å
El catalizador usado fue la tanda D preparada en p. 7

El catalizador fue pesado en una botella de boca ancha de 4 oz. y el 2-metil-3-butin-2-ol seco fue pesado en una botella de boca angosta de 500 ml. La botella del catalizador se llenó con una porción de la cantidad pesada de t-butinol, y se transfirió al reactor en B-4808 (Vicki Harrington). La botella del catalizador fue entonces enjuagada varias veces con t-butinol, transfiriéndose los lavados al reactor, seguido por el resto del t-butinol. El reactor fue entonces sellado y se desgasificó/purgó siete veces manualmente con nitrógeno (no se permitió que la presión cayera por debajo de la atmosférica para impedir pérdida del iniciador). La mezcla fue agitada y calentada a 90°C. La línea EO al reactor se drenó del nitrógeno para llenar la línea con EO. Una porción de EO (~50g) se agregó y la mezcla fue calentada y agitada mientras se vigilaba la presión del reactor para detectar el momento de iniciación de la reacción. Una pequeña caída de presión fue observada iniciándose unos 40 minutos después de la adición. Una hora después de la adición inicial, se agregó adicionalmente ~50g de EO y se vigiló la presión del reactor. La presión cayó más rápidamente y la velocidad de alimentación se colocó en modo automático. Esto causó que la velocidad de alimentación pasara por encima de 10g/min. A medida que la reacción progresó un exotérmico vigoroso se desarrolló, alcanzando un diferencial de más de 30°C desde la pared a la reacción. Esto hizo que el sistema se desestabilizara con cambios amplios en la temperatura de la camisa causando vaivenes amplios en la temperatura del reactor desde <80°C a más de 106°C durante periodos breves. El EO se alimentó rápido y la reacción fue digerida rápidamente. El material fue embotellado a ~20°C después de agitación durante la noche en el reactor y se obtuvo un color ámbar pálido. El material era opaco, pero permaneció líquido. Algunos asentamientos fueron observados. El análisis NMR mostró claramente que

el t-butinol inició la polimerización [cambio de =C de 89 ppm a 85 ppm]. El análisis GPC mostró 380 Mn, PDI de 1,82.

Fraccionamiento de la corrida 3 de t-butinol poliol: 5-13-99

El poliol (corrida 3 de t-butinol se inició [199900896- 12] ~1205g) fue suspendido con 2410g de alcohol isopropilo en un frasco de 6 l. El material fue agitado y se agregaron 1205 g de hexano. La mezcla fue agitada y enfriada en un baño de hielo durante varias horas. La mezcla fue luego filtrada en vacío por una almohadilla de media pulgada de auxiliar de filtro en un embudo de vidrio frito (basto). La corriente de líquido fue vertida sobre filtro de papel para facilitar la transferencia sin lavar el auxiliar de filtro. La solución clara fue concentrada por evaporación giratoria para proporcionar un líquido amarillo pálido. El peso del poliol de bajo Mn recuperado fue de 1078 g. El peso de la cera secada al aire fue de 109,09 g.

Preparación del catalizador:

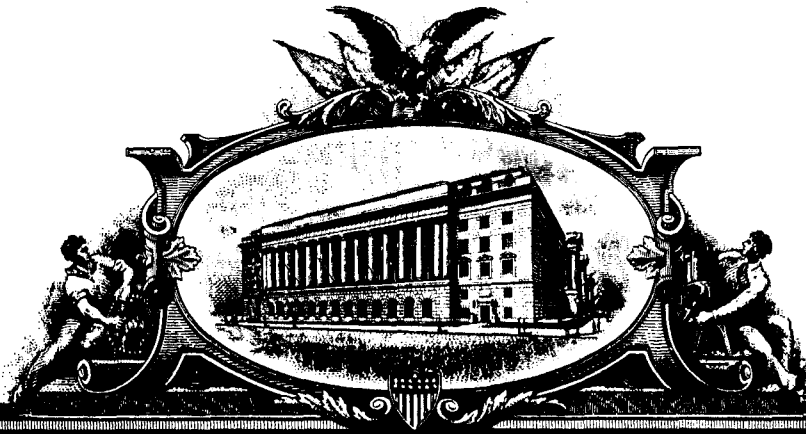
Hexacianocobaltato de potasio (8g) disuelto en 140 ml de agua desionizada (grado HPLC) [solución 1] fue agregado a un mezclador de una velocidad comercial (Waring Model 33BL79). Se energizó el mezclador y se agregó rápidamente cloruro de Cinc (25g) disuelto en 40 ml de agua [solución 2]. Se agregó una mezcla de 100 ml de agua y 100 ml de t-BuOH [solución 3] inmediatamente y la mezcla fue batida durante 10 minutos (la mezcla se calentó). La mezcla fue entonces enjuagada en un frasco de 1 litro con la solución A [2 g de CP-450 en 200 ml de agua] y se agitó durante cerca de 5 minutos, permitiendo que la mezcla se enfriara algo. Entonces la mezcla fue filtrada al vacío a través de 2 hojas de papel Whatman # 1 (no hubo pérdida de producto a través del filtro), enjuagando con cerca de 20 ml de agua DI. El ponqué húmedo se volvió a batir con la solución B [2 g de CP-450 en 140 ml de agua y 60 ml de t-BuOH] durante 3 minutos en una botella centrífuga y luego se centrifugo a 3000 rpm en la centrífuga Mistral 3000E durante 25 minutos. El líquido sobrenadante fue decantado y la mezcla fue resuspendida en la solución C [1 g de CP-450 en 200 ml de t-BuOH] durante varios minutos y luego se centrifugo. El líquido sobrenadante fue decantado y el sólido fue secado durante la noche a 75°C bajo vacío (30 Pulg.). Los sólidos secos fueron molidos en un mortero y triturador y se transfirió a un plato de cristalización para secado adicional hasta un peso constante. Producción 12,00 g.

COLO 00286-801-126-9

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THE UNITED STATES OF AMERICA

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UNITED STATES DEPARTMENT OF COMMERCE

United States Patent and Trademark Office

October 04, 2000

**THIS IS TO CERTIFY THAT ANNEXED HERETO IS A TRUE COPY FROM
THE RECORDS OF THE UNITED STATES PATENT AND TRADEMARK
OFFICE OF THOSE PAPERS OF THE BELOW IDENTIFIED PATENT
APPLICATION THAT MET THE REQUIREMENTS TO BE GRANTED A
FILING DATE UNDER 35 USC 111.**

APPLICATION NUMBER: 60/205,718

FILING DATE: May 19, 2000



**By Authority of the
COMMISSIONER OF PATENTS AND TRADEMARKS**

T. Wallace
T. WALLACE

Certifying Officer

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c777 U.S. PTO

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H/TINOV
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PROVISIONAL APPLICATION FOR PATENT COVER SHEET

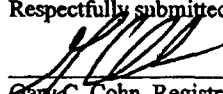
This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 CFR 1.53(c).

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☐ Additional inventors are named on the attached hereto.	
TITLE OF THE INVENTION (280 characters max) POLYMERIZATION OF ALKYLENE OXIDES ONTO FUNCTIONALIZED INITIATORS	
CORRESPONDENCE ADDRESS	
Direct all correspondence to: Gary C. Cohn GARY C. COHN PLLC 4010 Lake Washington Boulevard NE, Suite 105, Kirkland, WA 98033 (425) 576-1656 Fax: (425) 576-1756	
ENCLOSED APPLICATION PARTS	
☒ Specification, 16 pages	☐ Small entity statement
☐ Drawings, sheets	☐ Other
METHOD OF PAYMENT	
☐ A check or money order is enclosed to cover the filing fees. ☒ The commissioner is hereby authorized to charge filing fees or credit any overpayment to Deposit Account No. 04-1512	
FILING FEE AMOUNT: \$150	
☐ This invention was made by an agency of the United States Government or under a contract with an agency of the United States Government. The name of the U. S. Government agency and the Government contract number are:	

JC541 U.S. PTO
60/205718
05/19/00

Respectfully submitted,

Express Mail EJ740959925US

60205718-051980

Gary C. Cohn, Registration No. 30,456
(425) 576-1656
Date: May 19, 2000
Attorney Docket No. 60072

POLYMERIZATION OF ALKYLENE OXIDES ONTO FUNCTIONALIZED
INITIATORS

BACKGROUND OF THE INVENTION

5 This invention relates to processes for preparing poly(oxyalkylene) polymers and to methods for preparing same.

Polyethers made from alkylene oxides are well known and useful in a number of applications such as detergent and cleaner compositions, oil well drilling fluids, inks, metal working fluids, lubricants in paper coating compositions, ceramics
10 manufacturing, nonionic surfactants and chemical intermediates for nonionic surfactants which in turn are used in cosmetics, textiles and chemical processing, polyurethanes which are used as flexible foams, rigid foams and elastomers, manufacturing esters which are used in textile spin finishes, cosmetic agents, and as foam control agents for a wide variety of processes.. These polymers may have no
15 more than one oxyalkylene group in succession, or be a higher molecular weight polymer containing one or more long chains of consecutive oxyalkylene groups.

Polyethers of this type are commonly made through an anionic polymerization process, whereby the alkylene oxide is combined with an initiator compound and a strongly basic catalyst such as potassium hydroxide or certain organic amines is used.
20 The initiator compound contains one or more oxyalkylatable groups such as hydroxyl, thiol, carboxylate and the like. The initiator compound determines the functionality (i.e., number of hydroxyl groups/molecule of product) and in some cases may introduce some desired functional group into the product.

There are some disadvantages of polymerizing alkylene oxides using these
25 strongly basic catalysts. Some kinds of initiator compounds cannot be alkoxylated using strongly basic catalysts because they contain base-sensitive functional groups. Examples of these are halogenated initiators and initiators that contain nitro groups. In the presence of strong bases, halogens are removed from haloalcohol compounds. Nitroalcohols react in the presence of strong bases to form a variety of by-products. In
30 particular, nitro alcohols prepared via a Henry or Kamlet reaction or similar condensation of a nitroalkane with a carbonyl compound in the presence of base will undergo a retro reaction to generate the parent nitroalkane and carbonyl compound when exposed to basic conditions. These nitroalkane and carbonyl containing

products can then undergo further base catalyzed reactions to form more undesirable by-products.

In order to try to avoid these problems, Lewis acids such as boron trifluoride-diethyl etherate and organic amines such as triethyl amine have been tried.

5 However, some of these catalysts tend to promote the formation of large amounts of by-products, especially when it is attempted to add three or more moles of alkylene oxide per equivalent of initiator compound. The Lewis acid catalysts tend to catalyze "back-biting" reactions where the growing polymer chain reacts with itself. The reactions form cyclic ethers such as dioxane, substituted dioxane and various crown
10 ethers. These cannot be removed easily from the desired product, and so the product cannot be used in many applications.

Thus, it would be desirable to provide a method whereby polyethers made using halogenated or nitro-containing initiator compounds could be produced in good yield with low levels of by-products.

15

SUMMARY OF THE INVENTION

In one aspect, this invention is a process for preparing a polyether having one or more halogen or nitro groups, comprising forming a mixture of a halogenated or nitro-containing initiator compound having one or one oxyalkylatable groups, at least
20 one alkylene oxide and a metal cyanide catalyst complex, and subjecting the mixture to conditions sufficient to activate the catalyst complex and to alkoxylation the oxyalkylatable groups of the initiator.

In a second aspect, this invention is a poly(alkylene oxide) polymer containing the residue of an initiator compound containing at least one halogen or nitro group,
25 the polymer having an average alkoxy degree of polymerization of at least three moles of alkylene oxide per equivalent of initiator compound.

This invention permits the ready formation of polymers of initiators containing halogen or nitro substituents that do not survive base-catalyzed alkoxylation processes. The crude polymers made by this invention do not contain significant levels
30 of undesirable by-products such as nitroalkanes, carbonyl compounds, cyclic ethers and other impurities.

The polyether products of this process contain one or more terminal hydroxyl groups and at least one halogen or nitro group. The halogen or nitro functionality

provides a useful reactive site on the polyether through which various types of substituents can be formed. Of principal interest is the creation of amine functionality on the polyether to form a product having both hydroxyl and amine groups.

5 Thus, in additional aspects this invention includes processes for making polyethers that are both amine and hydroxyl-substituted. One of these processes comprises forming a mixture of a halogenated initiator compound having one or one oxyalkylatable groups, at least one alkylene oxide and a metal cyanide catalyst complex and subjecting the mixture to conditions sufficient to activate the catalyst
10 complex and to alkoxyate the oxyalkylatable groups of the initiator to form a polyether containing at least one halogen group and at least one hydroxyl group, and then contacting said polyether with ammonia, a primary amine or a secondary amine under conditions sufficient to replace said halogen group with an amine group.

Similarly, another such process comprises forming a mixture of a nitro-
15 containing initiator compound having one or one oxyalkylatable groups, at least one alkylene oxide and a metal cyanide catalyst complex and subjecting the mixture to conditions sufficient to activate the catalyst complex and to alkoxyate the oxyalkylatable groups of the initiator to form a polyether containing at least one nitro group and at least one hydroxyl group, and then subjecting said polyether to
20 conditions sufficient to reduce said nitro group to an amine group.

DETAILED DESCRIPTION OF THE INVENTION

In this invention, certain initiator compounds are alkoxyated by reaction with one or more alkylene oxides in the presence of a catalytically effective amount of a
25 metal cyanide catalyst. The alkoxylation is conducted by combining the initiator, metal cyanide catalyst and alkylene oxide. The catalyst is then allowed to become activated in the presence of the alkylene oxide. Once the catalyst has become activated, the mixture is subjected to conditions sufficient to polymerize the alkylene oxide. In this manner, the initiator compound becomes alkoxyated until
30 poly(oxyalkylene) chains of a desired length are introduced. As discussed below, once polymerization has begun, other types of monomers that are copolymerizable with alkylene oxides can be polymerized as well.

The initiator used herein contains at least one hydroxyl group that is bound to

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an aliphatic carbon atom and capable of being alkoxyated. The initiator also contains at least one halogen or nitro ($-\text{NO}_2$) group, either of which can be bound to either an aliphatic or aromatic carbon atom. Halogen groups include fluorine, chlorine, bromine and iodine, with chlorine and bromine being preferred. The initiator may contain
5 other functional groups as well, provided that they do not react in an undesirable way under the conditions of the alkoxylation reaction.

Suitable halogenated alcohols include 2-chloroethanol, 2-bromoethanol, 2-chloro-1-propanol, 3-chloro-1-propanol, 3-bromo-1-propanol, 1,3-dichloro-2-propanol, 1-chloro-2-methyl-2-propanol, 3-chloro-2,2-dimethyl-1-propanol, 3-bromo-2,2-
10 dimethyl-1-propanol, 4-chloro-1-butanol, 6-chloro-1-hexanol, 6-bromo-1-hexanol, 3-bromo-2-methyl-1-propanol, 7-bromo-1-heptanol, 8-chloro-1-octanol, 8-bromo-1-octanol, 2,2-dichloroethanol, 2,3-dibromopropanol, 2,2-bis(chloromethyl)-1-propanol, 2,2,2-tribromoethanol, 2,2,2-trichloroethanol, 2,2,2-trifluoroethanol, 2,2,3,3-tetrafluoro-1-propanol, 1-chloro-2-propanol, 1-bromo-2-propanol, 1,3-difluoro-2-
15 propanol, 1,3-dibromo-2-propanol, 1,4-dibromo-2-butanol, 3-chloro-1,2-propanediol, 3-bromo-1,2-propanediol, 2-chloro-2-propene-1-ol, 2-chlorocyclohexanol, alpha-(chloromethyl)2,4-dichlorobenzyl alcohol, and trans-2,3-dibromo-2-butene-1,4-diol. Suitable nitro alcohols include 2-nitro-2-methyl-1-propanol, 2-nitroethanol, 2-nitro-1-propanol, 3-nitro-2-butanol, 3-nitro-2-pentanol, 2-bromo-2-nitro-1,3-propanediol,
20 nitromethanetrispropanol, and tri(hydroxymethyl)nitromethane.

The alkoxylation is performed by first mixing the initiator, catalyst and an alkylene oxide and allowing the mixture to sit for a period of time at room or an elevated temperature. When these materials are mixed, a so-called induction period occurs, during which the oxyalkylene reaction occurs very slowly. The induction
25 period may range from a few minutes to several hours, depending on the particular catalyst that is used and the temperature. During this induction period, the catalyst becomes activated, and rapid polymerization of the alkylene oxide then commences.

The starting mixture of catalyst, initiator compound and alkylene oxide is conveniently made by combining the catalyst and initiator compound in a pressure
30 reactor (or by forming the catalyst in the initiator), and then pressurizing the reactor with an initial quantity of alkylene oxide. The induction period follows, as indicated by a nearly constant or slowly decreasing pressure in the reactor. The onset of rapid polymerization that follows the induction period is evidenced by a drop in pressure as

the alkylene oxide is consumed.

For halogenated initiators, the starting mixture of catalyst, initiator compound and alkylene oxide may be brought to any convenient temperature, such as from about 20°C, preferably from about 50°C, more preferably from about 70°C, even more preferably from about 80°C to about 150°C, preferably to about 130°C. These temperatures are also suitable for conducting the polymerization once the catalyst is activated. Somewhat lower temperatures are preferred when nitro-substituted initiators are used.

Depending on the desired degree of alkoxylation, all the necessary alkylene oxide may be added to the reactor at the outset. It is usually preferred to add more alkylene oxide to the reactor once the catalyst has become activated, especially when making higher molecular weight polyethers. A convenient way of adding the alkylene oxide is to pressurize the reactor with alkylene oxide and allow alkylene oxide to feed to the reactor on demand, maintaining a more or less constant pressure inside the reactor. Alternatively, any additional alkylene oxide may be fed in one or more discrete increments.

The total amount of alkylene oxide that is fed will depend on the desired equivalent weight of the product. As few as one mole of alkylene oxide per equivalent of initiator compound can be added. This invention is particularly suited for polymerizing at least about 3 moles of alkylene oxide per equivalent of initiator compound. Sufficient alkylene oxide can be added to make any desirable molecular weight polyether, such as one having a weight average molecular weight of 200,000 daltons or more. However, in most cases the intended end-use of the product will dictate its molecular or equivalent weight. For surfactant applications, molecular weights of from about 350 to about 6000 are of particular interest. In many applications, it is desirable that the product be a liquid. Poly(oxyethylene) homopolymers tend to form solids when their weight average molecular weights exceed about 1000 daltons. Thus, when a poly(ethylene oxide) homopolymer is made in accordance with the invention, preferred molecular weights are about 1000 or below. All weights reported above are number average molecular weights.

Similarly, the selection of alkylene oxide will depend to a large extent on the intended end-use of the product. Among the alkylene oxides that can be polymerized

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with the catalyst complex of the invention are ethylene oxide, propylene oxide, 1,2-butylene oxide, styrene oxide, and mixtures thereof. Mixtures of these can be used, and two or more of them can be polymerized sequentially to make block copolymers. For polyurethanes applications, preferred alkylene oxides are propylene oxide alone, mixtures of at least 50 weight % propylene oxide and up to about 50 weight % ethylene oxide (to form a random copolymer), and propylene oxide followed by ethylene oxide, so as to form terminal poly(oxyethylene) chains constituting up to about 30% of the total weight of the product. For other applications, ethylene oxide alone, 1,2-butylene oxide, ethylene oxide/1,2-butylene oxide mixtures, ethylene oxide followed by propylene oxide or butylene oxide, butylene oxide followed by ethylene and/or propylene oxide, propylene oxide alone, mixtures of propylene oxide and ethylene and/or butylene oxide, and propylene oxide followed by ethylene and/or butylene oxide are preferred alkylene oxides.

In addition, monomers that will copolymerize with the alkylene oxide in the presence of the catalyst complex can be used to prepare modified polyether polyols, after the catalyst has become activated. Such comonomers include oxetanes as described in U. S. Patent Nos. 3,278,457 and 3,404,109 and anhydrides as described in U. S. Patent Nos. 5,145,883 and 3,538,043, which yield polyethers and polyester or polyetherester polyols, respectively. Hydroxyalkanoates such as lactic acid, 3-hydroxybutyrate, 3-hydroxyvalerate (and their dimers), lactones as described in U. S. Patent No. 5,525,702 and carbon dioxide are examples of other suitable monomers that can be polymerized with the catalyst of the invention.

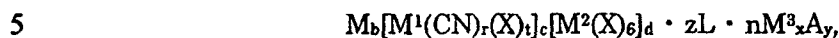
The polymerization reaction may be performed continuously or batchwise. In such continuous processes, initiator, catalyst and alkylene oxide are continuously fed into a continuous reactor such as a continuously stirred tank reactor (CSTR) or a tubular reactor. The product continuously removed.

The concentration of the catalyst is selected to polymerize the alkylene oxide at a desired rate or within a desired period of time. Generally, a suitable amount of catalyst is from about 5 to about 10,000 parts by weight metal cyanide catalyst complex per million parts of the product. For determining the amount of catalyst complex to use, the weight of the product is generally considered to equal the combined weight of alkylene oxide and initiator, plus any comonomers that may be used. More preferred catalyst complex levels are from about 10, especially from about

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25, to about 5000, more preferably about 1000 ppm, most preferably about 100 ppm, on the same basis.

The metal cyanide catalyst can be represented by the general formula:



wherein M is a metal ion that forms an insoluble precipitate with the $M^1(CN)_r(X)_t$ group and which has at least one water soluble salt;

M^1 and M^2 are transition metal ions that may be the same or different;

each X independently represents a group other than cyanide that coordinates with an

10 M^1 or M^2 ion;

L represents an organic complexing agent;

M^3A_y represents a water-soluble salt of metal ion M^3 and anion A, wherein M^3 is the same as or different than M;

b and c are positive numbers that, together with d, reflect an electrostatically neutral complex;

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d is zero or a positive number;

x and y are numbers that reflect an electrostatically neutral salt;

r is from 4 to 6; t is from 0 to 2;

z is zero or a positive number and n is a positive number indicating the relative quantities of the complexing agent and M^3A_y , respectively. z and n may be fractions.

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The X groups in any $M^2(X)_6$ do not have to be all the same. The molar ratio of c:d is advantageously from about 100:0 to about 20:80, more preferably from about 100:0 to about 50:50, and even more preferably from about 100:0 to about 80:20.

Similarly, the catalyst may contain two or more types of $M^1(CN)_r(X)_t$ groups and two or more types of $M^2(X)_6$ groups.

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M and M^3 are preferably metal ions selected from the group consisting of Zn^{+2} , Fe^{+2} , Co^{+2} , Ni^{+2} , Mo^{+4} , Mo^{+6} , Al^{+3} , V^{+4} , V^{+5} , Sr^{+2} , W^{+4} , W^{+6} , Mn^{+2} , Sn^{+2} , Sn^{+4} , Pb^{+2} , Cu^{+2} , La^{+3} and Cr^{+3} . M and M^3 are more preferably Zn^{+2} , Fe^{+2} , Co^{+2} , Ni^{+2} , La^{+3} and Cr^{+3} . M is most preferably Zn^{+2} .

Suitable anions A include halides such as chloride and bromide, nitrate, sulfate, carbonate, cyanide, oxalate, thiocyanate, isocyanate, perchlorate, isothiocyanate, and a C_{1-4} carboxylate. Chloride ion is especially preferred.

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M^1 and M^2 are preferably Fe^{+3} , Fe^{+2} , Co^{+3} , Co^{+2} , Cr^{+2} , Cr^{+3} , Mn^{+2} , Mn^{+3} , Ir^{+3} ,

00108
102

Ni⁺², Rh⁺³, Ru⁺², V⁺⁴ and V⁺⁵. Among the foregoing, those in the plus-three oxidation state are more preferred. Co⁺³ and Fe⁺³ are even more preferred and Co⁺³ is most preferred.

Preferred groups X include anions such as halide (especially chloride),
5 hydroxide, sulfate, C₁₋₄ carbonate, oxalate, thiocyanate, isocyanate, isothiocyanate, C₁₋₄ carboxylate and nitrite (NO₂⁻), and uncharged species such as CO, H₂O and NO. Particularly preferred groups X are NO, NO₂⁻ and CO.

The catalyst is usually complexed with an organic complexing agent. A great
10 number of complexing agents are potentially useful, although catalyst activity may vary according to the selection of a particular complexing agent. Examples of such complexing agents include alcohols, aldehydes, ketones, ethers, amides, nitriles, sulfides, and the like.

Suitable alcohols include monoalcohols and polyalcohols. Suitable
15 monoalcohols include methanol, ethanol, n-propanol, isopropanol, n-butanol, isobutanol, t-butanol, octanol, octadecanol, 3-butyne-1-ol, 3-butene-1-ol, propargyl alcohol, 2-methyl-2-propanol, 2-methyl-3-butyne-2-ol, 2-methyl-3-butene-2-ol, 3-butyne-1-ol, 3-butene-1-ol, 1-t-butoxy-2-propanol and the like. Suitable monoalcohols also include halogenated alcohols such as 2-chloroethanol, 2-bromoethanol, 2-chloro-1-propanol, 3-chloro-1-propanol, 3-bromo-1-propanol, 1,3-dichloro-2-propanol, 1-chloro-2-methyl-2-propanol as well as nitroalcohols, keto-alcohols, ester-alcohols,
20 cyanoalcohols, and other inertly substituted alcohols.

Suitable polyalcohols include ethylene glycol, propylene glycol, glycerine, 1,1,1-trimethylol propane, 1,1,1-trimethylol ethane, 1,2,3-trihydroxybutane, pentaerythritol, xylitol, arabitol, mannitol, 2,5-dimethyl-3-hexyne-2,5-diol, 2,4,7,9-
25 tetramethyl-5-decyne-4,7-diol, sucrose, sorbitol, alkyl glucosides such as methyl glucoside and ethyl glucoside, and the like. Low molecular weight polyether polyols, particular those having an equivalent weight of about 350 or less, more preferably about 125-250, are also useful complexing agents.

Suitable aldehydes include formaldehyde, acetaldehyde, butyraldehyde, valeric
30 aldehyde, glyoxal, benzaldehyde, toluic aldehyde and the like. Suitable ketones include acetone, methyl ethyl ketone, 3-pentanone, 2-hexanone and the like.

Suitable ethers include cyclic ethers such as dioxane, trioxymethylene and paraformaldehyde as well as acyclic ethers such as diethyl ether, 1-ethoxy pentane,

bis(betachloro ethyl) ether, methyl propyl ether, diethoxy methane, dialkyl ethers of alkylene or polyalkylene glycols (such as ethylene glycol dimethyl ether, diethylene glycol dimethyl ether, triethylene glycol dimethyl ether and octaethylene glycol dimethyl ether), and the like.

- 5 Amides such as formamide, acetamide, propionamide, butyramide and valeramide are useful complexing agents. Esters such as amyl formate, ethyl formate, hexyl formate, propyl formate, ethyl acetate, methyl acetate, triethylene glycol diacetate and the like can be used as well. Suitable nitriles include acetonitrile, proprionitrile and the like. Suitable sulfides include dimethyl sulfide, diethyl sulfide, 10 dibutyl sulfide, diamyl sulfide and the like.

- Preferred complexing agents are t-butanol, 1-t-butoxy-2-propanol, polyether polyols having an equivalent weight of about 75-350 and dialkyl ethers of alkylene and polyalkylene glycols. Especially preferred complexing agents are t-butanol, 1-t-butoxy-2-propanol, polyether polyols having an equivalent weight of 125-250 and a 15 dimethyl ether of mono-, di- or triethylene glycol. t-Butanol and glyme (1,2-dimethoxy ethane) are especially preferred.

- A silane-functional complexing agent, as described in the copending application of Wehmeyer entitled Method for Preparing Metal Cyanide Catalysts using Silane-functional Ligands, filed on even date herewith, may be used instead of 20 or in addition to the aforementioned complexing agents. As described therein, the silane-functional complexing agent may be polymerized to form a film or polymer, optionally on a support, or may function as a coupling agent to attach the catalyst complex to a support material.

- In addition, the catalyst complex often contains a quantity of water that is 25 bound into the crystalline lattice of the complex. Although the amount of bound water is difficult to determine, it is believed that this amount is typically from about 0.25 to about 3 moles of water per mole of M^1 and M^2 ions.

Exemplary catalysts include:

- Zinc hexacyanocobaltate $\cdot zL \cdot aH_2O \cdot nZnCl_2$;
 30 $Zn[Co(CN)_6NO] \cdot zL \cdot aH_2O \cdot nZnCl_2$;
 $Zn_s[Co(CN)_6]_o[Fe(CN)_6NO]_p \cdot zL \cdot aH_2O \cdot nZnCl_2$ (o, p = positive numbers, $s=1.5o + p$);
 $Zn_s[Co(CN)_6]_o[Co(NO_2)_6]_p[Fe(CN)_6NO]_q \cdot zL \cdot aH_2O \cdot nZnCl_2$ (o, p, q = positive

numbers, $s=1.5(o+p)+q$;

Zinc hexacyanocobaltate $\cdot zL \cdot aH_2O \cdot nLaCl_3$;

$Zn[Co(CN)_6NO] \cdot zL \cdot aH_2O \cdot nLaCl_3$;

$Zn[Co(CN)_6]_o[Fe(CN)_5NO]_p \cdot zL \cdot aH_2O \cdot nLaCl_3$ ($o, p =$ positive numbers, $s=1.5o + p$);

- 5 $Zn_s[Co(CN)_6]_o[Co(NO_2)_6]_p[Fe(CN)_5NO]_q \cdot zL \cdot aH_2O \cdot nLaCl_3$ ($o, p, q =$ positive numbers, $s=1.5(o+p)+q$);

Zinc hexacyanocobaltate $\cdot zL \cdot aH_2O \cdot nCrCl_3$;

$Zn[Co(CN)_5NO] \cdot zL \cdot aH_2O \cdot nCrCl_3$;

$Zn_s[Co(CN)_6]_o[Fe(CN)_5NO]_p \cdot zL \cdot aH_2O \cdot nCrCl_3$ ($o, p =$ positive numbers, $s=1.5o +$

- 10 p);

$Zn_s[Co(CN)_6]_o[Co(NO_2)_6]_p[Fe(CN)_5NO]_q \cdot zL \cdot aH_2O \cdot nCrCl_3$ ($o, p, q =$ positive numbers, $s=1.5(o+p)+q$);

Magnesium hexacyanocobaltate $\cdot zL \cdot aH_2O \cdot nZnCl_2$;

$Mg[Co(CN)_5NO] \cdot zL \cdot aH_2O \cdot nZnCl_2$;

- 15 $Mg_s[Co(CN)_6]_o[Fe(CN)_5NO]_p \cdot zL \cdot aH_2O \cdot nZnCl_2$ ($o, p =$ positive numbers, $s=1.5o + p$);

$Mg_s[Co(CN)_6]_o[Co(NO_2)_6]_p[Fe(CN)_5NO]_q \cdot zL \cdot aH_2O \cdot nZnCl_2$ ($o, p, q =$ positive numbers, $s=1.5(o+p)+q$);

Magnesium hexacyanocobaltate $\cdot zL \cdot aH_2O \cdot nLaCl_3$;

- 20 $Mg[Co(CN)_5NO] \cdot zL \cdot aH_2O \cdot nLaCl_3$;

$Mg_s[Co(CN)_6]_o[Fe(CN)_5NO]_p \cdot zL \cdot aH_2O \cdot nLaCl_3$ ($o, p =$ positive numbers, $s=1.5o + p$);

$Mg_s[Co(CN)_6]_o[Co(NO_2)_6]_p[Fe(CN)_5NO]_q \cdot zL \cdot aH_2O \cdot nLaCl_3$ ($o, p, q =$ positive numbers, $s=1.5(o+p)+q$);

- 25 Magnesium hexacyanocobaltate $\cdot zL \cdot aH_2O \cdot nCrCl_3$;

$Mg[Co(CN)_5NO] \cdot zL \cdot aH_2O \cdot nCrCl_3$;

$Mg_s[Co(CN)_6]_o[Fe(CN)_5NO]_p \cdot zL \cdot aH_2O \cdot nCrCl_3$ ($o, p =$ positive numbers, $s=1.5o + p$);

- 30 $Mg_s[Co(CN)_6]_o[Co(NO_2)_6]_p[Fe(CN)_5NO]_q \cdot zL \cdot aH_2O \cdot nCrCl_3$ ($o, p, q =$ positive numbers, $s=1.5(o+p)+q$);

as well as the various complexes such as are described at column 3 of U. S. Patent No. 3,404,109, incorporated herein by reference.

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The catalyst complex may be supported. One method of making a supported catalyst is by precipitating the catalyst in the presence of a polycarboxyl or polycarboxylate compound, as described in copending application of Wehmeyer entitled Method for Preparing Metal Cyanide Catalysts using Polycarboxylic Acids
5 filed on even date herewith. Supported catalysts as described in WO 99/44379 are also useful. In addition, supported catalysts can be prepared as described in the copending application of Wehmeyer entitled Method for Preparing Metal Cyanide Catalysts Using Silane-Functional Ligands, filed on even date herewith.

The catalyst complex is conveniently made using standard precipitation
10 methods as are described, for example, in U. S. Patent Nos. 3,278,457, 3,278,458, 3,278,459, 3,404,109, 3,427,256, 3,427,334, 3,427,335, 5,470,813, 5,482,908, 5,536,883, 5,589,431, 5,627,120, 5,627,122, 5,639,705, 5,714,428, 5,731,407, 5,780,584, 5,783,513, all incorporated herein by reference. In addition, the catalyst may be formed directly as a dispersion in an initiator compound, as described in copending application of
15 Wehmeyer, entitled Method for Preparing Metal Cyanide Catalyst/Polyol Initiator Slurries filed on even date herewith, or through an incipient wetness technique as described in the copending application of Molzahn et al, entitled Incipient Wetness Method for Making Metal-Containing Cyanide Catalysts, filed on even date herewith.

The product polyether is typically prepared in good yield with only small
20 amounts of undesired by-products. In some instances, the product may contain a high molecular weight "tail" that has a weight average molecular weight of 2X or more of that of the desired product. Typically, when this "tail" is present, it constitutes about 20% or less, more typically less than about 10% of the total weight of the product.

Other than the high molecular weight "tail", the process of the invention
25 permits the alkoxylation of halogenated and nitro-substituted initiator compounds with the formation of few by-products. By-products other than unreacted starting materials and the high molecular weight "tail" typically constitute less than about 10% by weight of the product, more typically less than about 5 weight percent and even more typically less than about 2 weight percent, prior to any clean-up or
30 purification. The product polyether is also generally characterized by having a good polydispersity, typically less than about 2.0, more typically less than about 1.25 and preferably less than about 1.05.

The product polyether contains at least one hydroxyl group and one or more

halogen or nitro groups. The halogen and nitro groups can be reacted with various reagents to introduce various types of functionality onto the polyether. Among these reactions, amination is of particular interest. Halogen atoms on the polyether can be reacted with ammonia, a primary amine or a secondary amine to introduce the corresponding amino group ($-\text{NH}_2$, $-\text{NHR}$ or $-\text{NR}_2$, respectively, where R is alkyl or aryl that may be substituted). Nitro groups are easily reduced using a variety of hydrogen sources, including gaseous hydrogen over a metal catalyst, hydrochloric acid over an iron catalyst, and hydrides such as lithium aluminum hydride

The following examples are provided to illustrate the invention, but are not
10 intended to limit its scope. All parts and percentages are by weight unless otherwise
indicated.

Example 1

1,3-Dichloro-2-propanol (0.1121 g), 6.2 mg of a zinc hexacyanocobaltate/t-butanol catalyst complex that has been treated with a 450 molecular weight poly(propylene oxide) triol are charged into a dried Wheaton vial fitted with a stir bar. The vial is sealed with a septum cap and purged with nitrogen. About 0.5 g of ethylene oxide are added by syringe and the septum cap is replaced with a solid cap under nitrogen. The vial is sealed and at 90°C for 14 hours. The product has an M_n of 690 and a polydispersity of 1.22. C^{13} NMR reveals that the resulting polyether contains chlorine atoms. The peak attributable to the chlorines is shifted slightly, indicating that the 1,3-dichloro-2-propanol has initiated the polymerization.

Example 2

2-chloroethanol (0.1161 g), 6.3 mg of a zinc hexacyanocobaltate/t-butanol catalyst complex that has been treated with a 450 molecular weight poly(propylene oxide) triol and 0.5 g ethylene oxide are charged into dried Wheaton vial fitted with a stir bar. The vial is sealed with a septum cap and purged with nitrogen. About 0.5 g of ethylene oxide are added by syringe and the septum cap is replaced with a solid cap under nitrogen. The vial is sealed and at 90°C for 14 hours. The product has an M_n of 530 and a polydispersity of 1.26. C^{13} NMR reveals that the resulting polyether contains chlorine atoms. The peak attributable to the chlorine is shifted slightly, indicating that the 2-chloroethanol has initiated the polymerization.

WHAT IS CLAIMED IS:

1. A process for preparing a polyether having one or more halogen or nitro groups, comprising forming a mixture of a halogenated or nitro-containing initiator compound having one or one oxyalkylatable groups, at least one alkylene oxide and a metal cyanide catalyst complex and subjecting the mixture to conditions sufficient to activate the catalyst complex and to alkoxyrate the oxyalkylatable groups of the initiator.
2. The process of claim 1 wherein the initiator compound is chlorinated or brominated.
3. The process of claim 2 wherein the alkylene oxide is ethylene oxide, propylene oxide or 1,2-butylene oxide.
4. The process of claim 3 wherein at least three moles of alkylene oxide are added per equivalent of initiator, and the polydispersity of the product is less than about 1.25.
5. The process of claim 5 wherein the initiator compound is 2-chloroethanol, 2-bromoethanol, 2-chloro-1-propanol, 3-chloro-1-propanol, 3-bromo-1-propanol, 1,3-dichloro-2-propanol, 1-chloro-2-methyl-2-propanol
6. The process of claim 1 wherein the initiator compound contains one or more nitro groups.
7. The process of claim 6 wherein the alkylene oxide is ethylene oxide, propylene oxide or 1,2-butylene oxide.
8. The process of claim 7 wherein at least three moles of alkylene oxide are added per equivalent of initiator, and the polydispersity of the product is less than about 1.25.

9. A poly(alkylene oxide) polymer containing the residue of an initiator compound containing at least one halogen or nitro group, the polymer having an average alkoxy degree of polymerization of at least three moles of alkylene oxide per equivalent of
5 initiator compound.

10. The polymer of claim 9 which contains, prior to any clean-up or purification, no more than 5 weight percent of by-products other than unreacted starting materials and a high molecular weight fraction.

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11. The process of claim 9 wherein the initiator compound is chlorinated or brominated.

12. The process of claim 10 wherein the alkylene oxide is ethylene oxide, propylene
15 oxide or 1,2-butylene oxide.

13. The process of claim 12 wherein at least three moles of alkylene oxide are added per equivalent of initiator, and the polydispersity of the product is less than about 1.25.

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14. The process of claim 13 wherein the initiator compound is 2-chloroethanol, 2-bromoethanol, 2-chloro-1-propanol, 3-chloro-1-propanol, 3-bromo-1-propanol, 1,3-dichloro-2-propanol, 1-chloro-2-methyl-2-propanol.

25 15. The process of claim 10 wherein the initiator compound contains one or more nitro groups.

16. The process of claim 11 wherein the alkylene oxide is ethylene oxide, propylene oxide or 1,2-butylene oxide.

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17. The process of claim 16 wherein at least three moles of alkylene oxide are added per equivalent of initiator, and the polydispersity of the product is less than about 1.25.

18. A process comprising forming a mixture of a halogenated initiator compound having one or one oxyalkylatable groups, at least one alkylene oxide and a metal cyanide catalyst complex and subjecting the mixture to conditions sufficient to
5 activate the catalyst complex and to alkoxyate the oxyalkylatable groups of the initiator to form a polyether containing at least one halogen group and at least one hydroxyl group, and then contacting said polyether with ammonia, a primary amine or a secondary amine under conditions sufficient to replace said halogen group with an amine group.
- 10
19. A process comprising forming a mixture of a nitro-containing initiator compound having one or one oxyalkylatable groups, at least one alkylene oxide and a metal cyanide catalyst complex and subjecting the mixture to conditions sufficient to
15 activate the catalyst complex and to alkoxyate the oxyalkylatable groups of the initiator to form a polyether containing at least one nitro group and at least one hydroxyl group, and then subjecting said polyether to conditions sufficient to reduce said nitro group to an amine group.

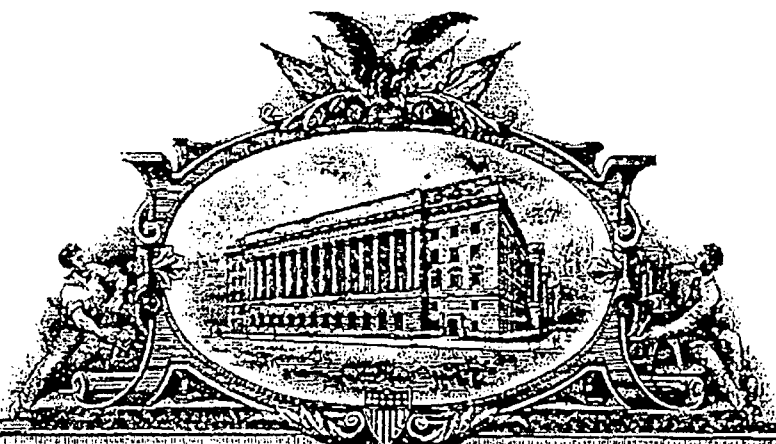
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ABSTRACT OF THE DISCLOSURE

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- 5 Certain alcohol initiators containing halogen or nitro substitution can be alkoxyated with excellent efficiency and low production of by-products using an metal cyanide catalyst. The products contain halogen or nitro groups that can undergo subsequent reactions to form amino groups.

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A TODO AQUEL A QUIEN CONCIERNA LO PRESENTE

DEPARTAMENTO DE COMERCIO DE LOS ESTADOS UNIDOS

Oficina de Patentes y Marcas de los Estados Unidos

04 de octubre de 2000

LA PRESENTE ES PARA CERTIFICAR QUE ADJUNTA A LA MISMA HAY UNA COPIA FIEL DE LOS REGISTROS DE LA OFICINA DE PATENTES Y MARCAS DE LOS ESTADOS UNIDOS DE LOS DOCUMENTOS DE LA SOLICITUD DE PATENTE IDENTIFICADA EN LO QUE SIGUE, QUE CUMPLEN LOS REQUISITOS PARA OTORGARLE UNA FECHA DE PRESENTACIÓN BAJO 35 USC 111.

NÚMERO DE SOLICITUD: 60/205,718

FECHA DE PRESENTACIÓN: 19 de mayo de 2000



Por la Autoridad del
COMISARIO DE PATENTES Y MARCAS

T. WALLACE
Oficial certificador

REIVINDICACIONES

1. Un proceso para prepara un poliéter que tiene uno o más grupos halógeno, aldehído, cetona o nitro, comprende formar una mezcla de un compuesto iniciador que contiene aldehído, halogenado, que contiene cetona o que contiene nitro y que tiene uno o más grupos oxialquilatables, por lo menos un óxido de alquileo y un complejo catalizador de cianuro de metal y someter la mezcla a condiciones suficientes para activar el complejo catalizador y para alcoxilar los grupos oxialquilatables del iniciador.
2. El proceso de la reivindicación 1 en donde el compuesto iniciador es clorinado o bromurado.
3. El proceso de la reivindicación 2 en donde el óxido de alquileo es óxido de etileno, óxido de propileno o 1,2-óxido de butileno.
4. El proceso de la reivindicación 3 en donde por lo menos 3 moles de óxido de alquileo son agregadas

por equivalente de iniciador, y la polidispersidad del producto es menor a 1,25.

5. El proceso de la reivindicación 5 en donde el compuesto iniciador es 2-cloroetanol, 2-bromoetanol, 2-cloro-1-propanol, 3-cloro-1-propanol, 3-bromo-1-propanol, 1,3-dicloro-2-propanol, 1-cloro-2-metil-2-propanol.
6. El proceso de la reivindicación 1 en donde el compuesto iniciador contiene uno o más grupos nitro.
7. El proceso de la reivindicación 6 en donde el óxido de alquileo es óxido de etileno, óxido de propileno o óxido de 1,2-butileno.
8. El proceso de la reivindicación 7 en donde por lo menos 3 moles de óxido de alquileo se agregan por equivalente de iniciador, y la polidispersidad del producto es menor a 1,25.
9. Un polímero de poli(óxido de alquileo) contiene el residuo de un compuesto iniciador que contiene

por lo menos un grupo halógeno, aldehído cetona o nitro, el polímero tiene un grado alcoxi promedio de polimerización de por lo menos tres moles de óxido de alquileo por equivalente del compuesto iniciador.

10. El polímero de la reivindicación 9 que contiene, antes de cualquier limpieza o purificación, no más de 5% en peso de productos intermedios diferentes que reaccionan de los materiales de partida y de fracciones de alto peso molecular.
11. El proceso de la reivindicación 9 en donde el compuesto iniciador es clorinado o bromurado.
12. El proceso de la reivindicación 10 en donde el óxido de alquileo es óxido de óxido de etileno, óxido de propileno u óxido de 1,2-butileno.
13. El proceso de la reivindicación 12 en donde por lo menos tres moles de óxido de alquileo son agregados por equivalente de iniciador, y la polidispersidad del producto es menor a 1,25.

14. El proceso de la reivindicación 13 en donde el compuesto iniciador es 2-cloroetanol, 2-bromoetanol, 2-cloro-1-propanol, 3-cloro-1-propanol, 3-bromo-1-propanol, 1,3-dicloro-2-propanol, 1-cloro-2-metil-2-propanol.
15. El proceso de la reivindicación 10 en donde el compuesto iniciador contiene uno o más grupos nitro.
16. El proceso de la reivindicación 11 en donde el óxido de alquileo es óxido de etileno, óxido de propileno, u óxido de 1,2-butileno.
17. El proceso de la reivindicación 16 en donde por lo menos 3 moles de óxido de alquileo son agregados por equivalente de iniciador, y la polidispersidad de producto es menor a 1,25.
18. Un proceso que comprende la formación de una mezcla de un compuesto iniciador halogenado que tiene uno o más grupo oxialquilatables, por lo menos un óxido de alquileo y un complejo catalizador de cianuro de metal y someter la

mezcla a condiciones suficientes para activar el complejo catalizador y para alcoxilar los grupos oxialquilatables del iniciador para formar un poliéter que contiene por lo menos un grupo halógeno y por lo menos un grupo hidroxilo, y luego poner en contacto dicho poliéter con amoniaco, una amina primaria o una amina secundaria bajo condiciones suficientes para reemplazar dicho grupo halógeno con un grupo amino.

19. Un proceso que comprende formar una mezcla de un compuesto iniciador que contiene nitro que tiene uno o más grupos oxialquilatables, por lo menos un óxido de alquileo y una complejo catalizador de cianuro de metal y someter la mezcla a condiciones suficientes para activar el complejo catalizador y para alcoxilar los grupos oxialquilatables del iniciador para formar un poliéter que contiene por lo menos un grupo nitro y por lo menos un grupo hidroxilo, y luego someter dicho poliéter a condiciones suficientes para reducir dicho grupo nitro en un grupo amina.