PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 :
C07F 9/6574 // C08K 5/527, 5/5333

A1

(11) International Publication Number: WO 96/35694

(43) International Publication Date: 14 November 1996 (14.11.96)

(21) International Application Number: PCT/EP96/01914

(22) International Filing Date: 3 May 1996 (03.05.96)

(30) Priority Data:
08/438,152 9 May 1995 (09.05.95) US

(71) Applicant: AKZO NOBEL N.V. [NL/NL]; Velperweg 76, NL-6824 BM Arnhem (NL).

(72) Inventor: TELSCHOW, Jeffrey, Earl; 416 Benedict Avenue, Tarrytown, NY 10591 (US).

(74) Agent: SCHALKWIJK, Pieter, Cornelis; Akzo Nobel N.V., Patent Dept. (Dept. APTA), P.O. Box 9300, NL-6800 SB Arnhem (NL).

(81) Designated States: CA, CN, JP, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published
With international search report.

(54) Title: (PENTAERYTHRITOL PHOSPHATE ALCOHOL) (CYCLIC NEOPENTYLENE GLYCOL) PHOSPHITE AND PHOSPHONATE

(57) Abstract

(Pentaerythritol phosphate alcohol) (cyclic neopentylene glycol) phosphite and phosphonate are disclosed as flame retardant compounds. The first named compound is formed by the reaction of pentaerythritol phosphate alcohol with a neopentylene glycol halophosphite, such as neopentylene glycol chlorophosphite. The (pentaerythritol phophate alcohol) (cyclic neopentylene glycol) phosphonate is formed by heating (pentaerythritol phosphate alcohol) (cyclic neopentylene glycol) phosphite.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	**GB**	United Kingdom	**MW**	Malawi
AT	Austria	**GE**	Georgia	**MX**	Mexico
AU	Australia	**GN**	Guinea	**NE**	Niger
BB	Barbados	**GR**	Greece	**NL**	Netherlands
BE	Belgium	**HU**	Hungary	**NO**	Norway
BF	Burkina Faso	**IE**	Ireland	**NZ**	New Zealand
BG	Bulgaria	**IT**	Italy	**PL**	Poland
BJ	Benin	**JP**	Japan	**PT**	Portugal
BR	Brazil	**KE**	Kenya	**RO**	Romania
BY	Belarus	**KG**	Kyrgystan	**RU**	Russian Federation
CA	Canada	**KP**	Democratic People's Republic of Korea	**SD**	Sudan
CF	Central African Republic			**SE**	Sweden
CG	Congo	**KR**	Republic of Korea	**SG**	Singapore
CH	Switzerland	**KZ**	Kazakhstan	**SI**	Slovenia
CI	Côte d'Ivoire	**LI**	Liechtenstein	**SK**	Slovakia
CM	Cameroon	**LK**	Sri Lanka	**SN**	Senegal
CN	China	**LR**	Liberia	**SZ**	Swaziland
CS	Czechoslovakia	**LT**	Lithuania	**TD**	Chad
CZ	Czech Republic	**LU**	Luxembourg	**TG**	Togo
DE	Germany	**LV**	Latvia	**TJ**	Tajikistan
DK	Denmark	**MC**	Monaco	**TT**	Trinidad and Tobago
EE	Estonia	**MD**	Republic of Moldova	**UA**	Ukraine
ES	Spain	**MG**	Madagascar	**UG**	Uganda
FI	Finland	**ML**	Mali	**US**	United States of America
FR	France	**MN**	Mongolia	**UZ**	Uzbekistan
GA	Gabon	**MR**	Mauritania	**VN**	Viet Nam

(PENTAERYTHRITOL PHOSPHATE ALCOHOL) (CYCLIC NEOPENTYLENE GLYCOL) PHOSPHITE AND PHOSPHONATE

Background of the Invention

Various derivatives of pentaerythritol phosphate are known as flame retardant additives for polymers such as polypropylene. A recent example is provided by U.S. Patent No. 4,801,625 to W.J. Parr et al. which describes ether, ester and carbonate derivatives of pentaerythritol phosphate. The carbonate version of such compounds can be advantageously prepared by the reaction of pentaerythritol phosphate alcohol with a dihydrocarbyl carbonate as described in U.S. Patent No. 5,235,085.

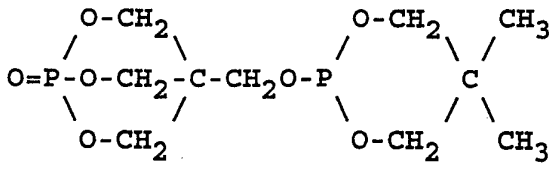
Summary of the Invention

The invention relates to (pentaerythritol phosphate alcohol) (cyclic neopentylene glycol)phosphite and (pentaerythritol phosphate alcohol) (cyclic neopentylene glycol) phosphonate which are useful as flame retardant compounds. The first named compound is formed by the reaction of pentaerythritol phosphate alcohol ("PEPA") with a neopentylene glycol halophosphite, such as neopentylene glycol chlorophosphite. The (pentaerythritol phosphate alcohol) (cyclic neopentylene glycol) phosphonate is formed by heating (pentaerythritol phosphate alcohol) (cyclic neopentylene glycol) phosphite.

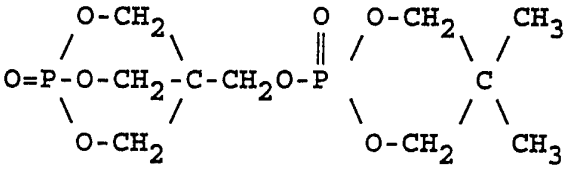
U.S. Patent No. 5,362,898 discloses certain bis(pentaerythritol phosphate alcohol) alkylphosphonate compounds, such as those containing from about one to about four carbon atoms in their alkyl moiety, with bis(pentaerythritol phosphate alcohol) methylphosphonate being a preferred species thereof.

Description of the Preferred Embodiments

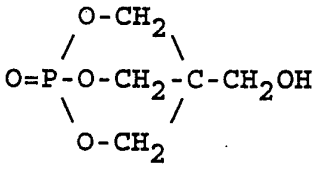
The present novel (pentaerythritol phosphate alcohol) (cyclic neopentylene glycol) phosphite compound is of the formula:



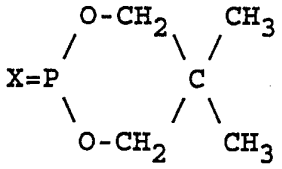
and the novel (pentaerythritol phosphate alcohol) (cyclic neopentylene glycol) phosphonate compound is of the formula:



One process for forming the above-described novel phosphite compound is by the reaction of a neopentylene glycol halophosphite with pentaerythritol phosphate alcohol which has the formula:



The neopentylene glycol halophosphite reagent is of the formula:



where X is a halogen atom, such as chlorine. The reaction can be conducted at room temperature in an appropriate organic solvent, such as acetonitrile using an acid acceptor, such as a trialkylamine.

Once the phosphite compound has been synthesized, it can be converted to the novel phosphonate compound of the present invention by heating, for example, in a high boiling organic solvent, such as an aryl phosphate solvent.

The present invention is further understood by reference to the Examples which follow.

EXAMPLE 1

In a 250 mL, mechanically stirred, four-necked flask fitted with pot thermometer, condenser and dropping funnel were placed 18.0 grams (0.10 mole) of pentaerythritol phosphate alcohol (PEPA), 13.9 mL (10.1 grams, 0.10 mole) of triethylamine, and 75 ml of dry acetonitrile. Then, 16.9 grams (0.10 mole) of neopentylene chlorophosphite (2-chloro-5,5-dimethyl-1,3,2-dioxaphosphorinane) was added dropwise from the funnel over twenty minutes, while maintaining the temperature of the stirred reaction mixture at 20-30°C under nitrogen. The mixture was allowed to stir for twenty-two hours at ambient temperature, the white solid which had formed was filtered and was dissolved in 300 mL of methylene chloride and was then extracted three times with 100 mL of water. On evaporation of the methylene chloride, 4.1 grams of a white powder with a melting point of 200-203°C remained. The solid exhibited two equally intense singlets by ^{31}P NMR (d_6-DMSO) at +122.7 and -6.2 ppm, consistent with the desired PEPA-NPG phosphite product (5,5-dimethyl-2-(2-oxo-2,6,7-trioxa-1-phosphabicyclo[2.2.2]oct-4-yl-methoxy)-1,3,2-dioxaphosphorinane).

EXAMPLE 2

In a 100 mL, mechanically stirred, four-necked flask fitted with pot thermometer, were placed 11.4 grams (0.0367 mole) of the PEPA-NPG phosphite from Example 1, 20 mg of iodine, and 30 mL of Phosflex® 41P under nitrogen. The solution was heated for sixteen hours at 210°C to promote Arbuzov rearrangement. Analysis using ^{31}P NMR (d_6-DMSO) revealed two resonances at +19.3 and -7.1 ppm, corresponding to the desired PEPA-NPG phosphonate product (5,5-dimethyl-2-(2-oxo-2,6,7-trioxa-1-phospha-bicyclo[2.2.2]oct-4-ylmethyl)-1,3,2-dioxaphosphorinane, 2-oxide).

The foregoing Examples are intended to illustrate certain embodiments of the present invention and, for that reason, should not be construed in a limiting sense. The scope of protection sought is set forth in the claims which follow.

Claims

1. (Pentaerythritol phosphate alcohol) (cyclic neopentylene glycol) phosphite.
2. (Pentaerythritol phosphate alcohol) (cyclic neopentylene glycol) phosphonate.

INTERNATIONAL SEARCH REPORT

International Application No
PC./EP 96/01914

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C07F9/6574 //C08K5/527,C08K5/5333

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C07F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US,A,3 883 478 (GRESHAM JOHN T) 13 May 1975 cited in the application see the whole document ---	1,2
Y	US,A,5 362 898 (TELSCHOW JEFFREY E) 8 November 1994 cited in the application see the whole document ---	1,2
Y	FR,A,2 342 984 (BORG WARNER) 30 September 1977 see the whole document ---	1,2
Y	WO,A,92 16537 (ETHYL CORP) 1 October 1992 see the whole document ---	1,2
	-/--	

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

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

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

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

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

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
11 July 1996	30.08.96

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax (+31-70) 340-3016	Beslier, L

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 96/01914

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,Y	US,A,5 420 326 (TELSCHOW JEFFREY E) 30 May 1995 see the whole document -----	1,2

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

nformation on patent family members

International Application No
PC./EP 96/01914

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-3883478	13-05-75	US-A- 3944633	16-03-76
US-A-5362898	08-11-94	WO-A- 9514704	01-06-95
		US-A- 5486640	23-01-96
		US-A- 5486639	23-01-96
FR-A-2342984	30-09-77	CA-A- 1078862	03-06-80
		DE-A- 2709528	15-09-77
		DE-C- 2759879	18-10-84
		GB-A- 1526603	27-09-78
		JP-C- 1639247	18-02-92
		JP-A- 52106879	07-09-77
		JP-B- 59021343	19-05-84
		NL-A,B,C 7701928	06-09-77
		SU-A- 917698	30-03-82
		US-A- 4305866	15-12-81
WO-A-9216537	01-10-92	NONE	
US-A-5420326	30-05-95	WO-A- 9531465	23-11-95