

## General Disclaimer

### One or more of the Following Statements may affect this Document

- This document has been reproduced from the best copy furnished by the organizational source. It is being released in the interest of making available as much information as possible.
- This document may contain data, which exceeds the sheet parameters. It was furnished in this condition by the organizational source and is the best copy available.
- This document may contain tone-on-tone or color graphs, charts and/or pictures, which have been reproduced in black and white.
- This document is paginated as submitted by the original source.
- Portions of this document are not fully legible due to the historical nature of some of the material. However, it is the best reproduction available from the original submission.

METHOD OF REFINING 2,2-ISOPROPYLIDENE BIS-3,5-DIBROMOPHENYLENE-4-OXYDIETHANOL

Takayuki Kobayashi, Kiyoshi Nawata, Kyuo Hiratsuka



Translation of Japanese Patent No. 51-63161 (1976) to Takayuki Kobayashi; Applicant Teijin K.K.; IPC C C 07 C 43/20; Date of Application, November 26, 1974; Date of Disclosure, June 1, 1976; Japanese Title: 2,2-isopropiridenbis-3,5-jiburomofueniren-4-okishijietanoru no seiseiho

(NASA-TM-77458) METHOD OF REFINING N84-19492  
2,2-ISOPROPYLIDENE BIS-3,5-  
DIBROMOPHENYLENE-4-OXYDIETHANOL (National  
Aeronautics and Space Administration) 7 p Unclas  
HC A02/MF A01 CSCL 07D G3/25 12471

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION  
WASHINGTON, DC 20546 JULY 1982

1. Report Number NASW-77458	2. Government Accession No.	3. Secondary Number
4. Title and Subtitle METHOD OF REFINING 2,2-ISO- PROPYLIDENE BIS-3,5-DIBROMOPHENYLENE-4- OXYDIETHANOL	5. Date July 1982	6. Distribution Statement
7. Author(s) T. Kobayashi, K. Nawata and K. Hiratsuka	8. Performing Organization Name(s)	9. Performing Organization Address
10. Performing Organization Report Number	11. Contract Grant Number NASW-3541	12. Type of Report and Period Covered translation
13. Sponsoring Agency Name and Address Leo Kanner Associates Redwood City California 94063	14. Sponsoring Agency Code	
15. Supplementary Notes Translation of "2,2-isopropylidenebis-3,5-dibromo- phenylene-4-oxidiethanol is described which is characterized by recrystallization of 2,2-isopropylidenebis-3,5-dibromo- phenylene-4-oxidiethanol using one or more aromatic hydrocarbons such as benzene, xylene, toluene, ethylbenzene or pseudo- cumene.		

Unclassified - Unlimited

Unclassified

Unclassified

METHOD OF REFINING 2,2-ISOPROPYLIDENEBIS-3,5-DIBROMOPHENYLENE-4-OXYDIETHANOL

Takayuki Kobayashi, Kiyoshi Nawata, Kyo Hiratsuka

1. Title of Invention

/431\*

Method of refining 2,2-isopropylidenebis-3,5-dibromophenylene-4-oxydiethanol.

2. Scope of Patent Claim

A method of refining 2,2-isopropylidenebis-3,5-dibromophenylene-4-oxydiethanol characterized by recrystallization of 2,2-isopropylidenebis-3,5-dibromophenylene-4-oxydiethanol using one or more aromatic hydrocarbons such as benzene, xylene, toluene, ethylbenzene or pseudocumene.

3. Detailed Description of the Invention

This invention relates to a method of producing 2,2-isopropylidenebis-3,5-dibromophenylene-4-oxydiethanol (below abbreviated Br compound, specifically to a method of refining Br compounds illustrated by the following structural formula

insert formula

which is capable of imparting a high degree of incombustibility to linear or unsaturated polyester.

Incombustible polyesters can be produced through additive copolymerization of Br compounds during linear polymerization of linear polyester, for example, as is well known. There is a pronounced tendency for coloration due to slight amounts of impurities contained in said Br compounds since said incombustible polyester has a history of extreme heating in the course of production.

"Numbers in the margin indicate pagination of the foreign text."

Consequently, a very high degree of refining of Br compounds is required to produce very incombustible polyester with high commercial value using said Br compounds.

The inventors have conducted thorough research into methods of refining the aforementioned Br compounds with very high purity, the result of which was the discovery that said conditions could be satisfied by recrystallization refining of Br compounds using a specific aromatic compound as the recrystallization solvent, thereby completing this invention.

/432

Specifically, this invention provides a method of refining 2,2-isopropylidenebis-3,5-dibromophenylene-4-oxydiethanol characterized by recrystallization of 2,2-isopropylidenebis-3,5-dibromophenylene-4-oxydiethanol using one or more aromatic hydrocarbons such as benzene, xylene, toluene, ethylbenzene or pseudocumene.

The Br compound used in this invention may be that which is produced by any method. For example, it may be produced through reaction of tetrabromobisphenol A produced through nuclear bromination of bisphenol A with ethylene oxide, or it may be produced through reacting tetrabromobisphenol A and ethylene chlorohydrin in the presence of alkali.

Among the aforementioned aromatic hydrocarbons used in recrystallization, benzene and toluene are interesting in terms of their solubility and the purity of the refined product. The recrystallization solvent is restricted to specific aromatic hydrocarbons, and the raw materials present in slight quantities in the Br compounds as well as tetrabromobisphenol A and its monohydroxyethyl ether etc. which are intermediate products can be effectively removed through suitable selection of the solvent. Aliphatic hydrocarbons and alcohols, which are general

recrystallization solvents in addition to these aromatic hydrocarbons, do not completely remove the impurities even when used as recrystallization solvents of Br compounds, and they cannot be used in the recrystallization methods of this invention.

The amounts of the aforementioned aromatic hydrocarbons used vary with the type, but usually 0.5 to 10-fold parts (weight parts), preferably 1 to 5-fold parts (weight parts) in relation to the coarse Br compounds to be recrystallized would be used.

Recrystallization using the aforementioned aromatic hydrocarbons is conducted at normal temperature. Specifically, coarse Br compounds are heated and dissolved in the aforementioned aromatic hydrocarbons, and the insoluble materials are heated and removed. Refined Br compounds are crystallized and precipitated by then cooling the mother liquor. At this time, the dissolution temperature would vary with the type of solvent, and the optimum dissolution temperatures would be 60 to 80°C for benzene, 90 to 110°C for xylene, 80 to 100°C for toluene, 90 to 110°C for ethyl benzene and 100 to 120°C for pseudocumene. In addition, the cooling temperature as well varies with the type of solvent used, and the optimum cooling temperatures are 20 to 30° for benzene, 25 to 35°C for xylene, 15 to 35°C for toluene, 30 to 40°C for ethyl benzene and 30 to 40°C for pseudocumene.

Effective results would be realized with no obstacles through the use of adsorbents such as active carbon, silica gel, alumina etc. in the implementation of this invention to raise the purification effects.

This invention is detailed below through actual examples, but the invention is not restricted to the following actual

examples. In the example, "parts" always refers to weight parts while " $\eta$ " always refers to the ultimate viscosity determined from measurement in orthochlorphenol at 35°C. The softening point was determined by the penetration method using a softening point measurement device. The b value indicating the color of the polyester produced is the measurement using the Hunter type optical densitometer. This b value indicates that the yellow color exhibited was intense, and a value above 10 is unacceptable.

Actual Examples 1-5 and Comparative Examples 1,2

(a) 544 parts of tetrabromobisphenol A, 242 parts of ethylene chlorohydrin and 120 parts of caustic soda were reacted to produce 63.2 parts of 2,2-isopropylidenebis-3,5-dibromophenol-4-oxydiethanol which was added to the solvents mentioned in table 1, heated and dissolved under the conditions illustrated in the table. Subsequently, slight amounts of undissolved substances remaining were removed by heating and filtration. The filtrate was cooled to the temperatures mentioned in the table, and the precipitated crystals were filtered off, followed by decompression drying at 20 mmHg, 60°C. The color, melting point and the results of observation of the resulting crystals under a polarized light microscope are as illustrated in table 1.

(b) 14.5 parts of the 2,2-isopropylidenebis-3,5-dibromophenylene-4-oxydiethanol obtained in this fashion, 97 parts of dimethylterephthalate, 67 parts of ethylene glycol and 0.088 parts of calcium acetate as a catalyst were introduced into a reaction vessel fitted with an agitator, refining tower and precipitation condenser, followed by heating from 140°C to 225°C and reaction while distilling off the methanol produced as a result of the ester exchange reaction. 32 parts of methanol were distilled off approximately 3 hours after the start of the reaction. The reaction was terminated at this point, and the

reaction blend was transferred to a condensation polymerization reaction vessel fitted with an agitator and glycol distillation condenser. The normal pressure reaction was conducted for 30 minutes at 260°C, for 30 minutes at a slight vacuum of 20 mmHg and for 10 minutes under pressure reduction from 20 mmHg to 3 mmHg. The condensation polymerization reaction was then implemented under high vacuum of 0.3 mm Hg at 275°C for 60 minutes. Table 1 illustrates the limiting viscosity, the softening point and the color of the resulting polyester. The resulting polymers were then recrystallized for three hours at 140°, and the b values measured using a Hunter type optical densitometer are also illustrated in table 1. Furthermore, these polymers were all self-extinguishing.

Table 1

	1 溶剤		3 量 (部)	5 冷却温度		4 溶解温度 (°C)	6 精製		9 偏光顕微鏡による観察結果	10 ポリエステル	12 色	
	2 種類	種類		7 色	8 融点 (°C)		11 軟化点 (°C)	13 顕微鏡			14 b	
14 実例	16	17	150	75	20	23	110-112	112°Cで完全結晶化	0.65	2480	27	7.12
	18	17	150	100	25	23	110-112	25	0.65	2480	27	8.05
	19	17	200	55	35	24	110-112	24	0.64	2485	27	8.54
	20	17	200	100	35	24	110-112	24	0.65	2487	27	8.78
	21	17	200	100	35	24	110-112	24	0.66	2485	27	8.90
15 比較例	22	17	70	45	10	23	107-110	120°Cで少量結晶化が認められる	0.65	2485	27	11.58
	22	17	150	80	10	23	108-115	120°Cで少量結晶化が認められる	0.64	2482	27	11.60

- |   |   |
|---|---|
| 1 solvent   | 2 type  |
| 3 amount (parts)  | 4 dissolution temperature                             |
| 5 cooling temperature                                     | 6 refined material                                    |
| 7 color   | 8 melting point                                       |
| 9 results of observation using polarized light microscope | 10 polyester product                                  |
| 11 softening point  | 12 color  |
| 13 macroscopic  | 14 actual example                                     |
| 15 comparative example                                    | 16 benzene  |
| 17 toluene  | 18 blended xylene                                     |
| 19 ethyl benzene  | 20 pseudocumene                                       |
| 21 methanol   | 22 cyclohexanone                                      |
| 23 colorless  | 24 pale yellow  |
| 25 no crystallization at 112°C                            | 26 slight amounts of crystallization evident at 120°C |
| 27 pale yellow  |   |