



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

|  |  |   |   |
|--|--|---|---|
| (51) International Patent Classification <sup>6</sup> :<br><br>C08G 63/88  |  | A1  | (11) International Publication Number: <b>WO 98/18848</b><br><br>(43) International Publication Date: 7 May 1998 (07.05.98) |
| (21) International Application Number: PCT/US97/19403<br><br>(22) International Filing Date: 28 October 1997 (28.10.97)  |  | (81) Designated States: AU, BR, CA, CN, CZ, HU, ID, IL, JP, KR, MX, NO, NZ, PL, RU, SG, SK, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).                       |   |
| (30) Priority Data:<br>60/028,625 28 October 1996 (28.10.96) US<br>08/956,670 23 October 1997 (23.10.97) US  |  | <b>Published</b><br><i>With international search report.</i><br><i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i> |   |
| (71) Applicant: EASTMAN CHEMICAL COMPANY [US/US];<br>100 North Eastman Road, Kingsport, TN 37660 (US).   |  |   |   |
| (72) Inventors: NELSON, Gregory, Wayne; 4814 Preston Park Drive, Kingsport, TN 37664 (US). NICELY, Vincent, Alvin; 2605 Suffolk Street, Kingsport, TN 37660 (US). TURNER, Sam, Richard; 1037 Sussex Drive, Kingsport, TN 37660 (US). |  |   |   |
| (74) Agent: HARDING, Karen, A.; P.O. Box 511, Kingsport, TN 37662-5075 (US).   |  |   |   |

(54) Title: PROCESS FOR PRODUCING PET ARTICLES WITH LOW ACETALDEHYDE

## (57) Abstract

The present invention discloses a process for producing molded, shaped or extruded articles comprising the steps of: a) melt reacting, in the presence of a catalyst which is substantially free of Co compounds, at least one glycol and at least one dicarboxylic acid to form a polyester having an I.V. of at least about 0.5 dL/g, wherein said at least one glycol is selected from the group consisting of glycols having up to 10 carbon atoms and mixtures thereof and said dicarboxylic is selected from the group consisting of alkyl dicarboxylic acids having 2 to 16 carbon atoms, aryl dicarboxylic acids having 8 to 16 carbon atoms and mixtures thereof; b) adding an acetaldehyde reducing additive to said polyester to form a reduced acetaldehyde polyester; and c) forming said reduced acetaldehyde polyester into articles directly from step b. Thus, the present invention provides a process for directly producing from the melt article having extremely low acetaldehyde content.

**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.

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

- 1 -

PROCESS FOR PRODUCING PET ARTICLES  
WITH LOW ACETALDEHYDE

This application is based upon and claims the  
5 priority of provisional application 60/028,625 filed  
October 28, 1996.

Background of the Invention

Polyesters are widely used in the manufacture of  
10 fibers, molded objects, films, sheeting, food trays, as  
well as food and beverage containers. These polymers are  
generally made by batch or continuous melt phase  
polycondensation reactions well known in the art. The  
polymers are then pelletized and used in various  
15 extrusion or molding operations. In certain  
applications where higher molecular weight polymers are  
required, the pellets are subjected to "solid state"  
polycondensation conditions in which the inherent  
viscosity (I.V.) value is significantly increased. Such  
20 solid state polycondensation reactions are used for two  
reasons. First, because the melt viscosity of polyester  
polymers is quite high for polymers having I.V. values  
greater than about 0.6, solid stating provides a  
convenient means to handle the polymer. Secondly, the  
25 solid stating process provides conditions conducive to  
removing unwanted volatile impurities such as  
acetaldehyde which is important in certain applications.  
Also, polyesters are well known to be degraded by small  
amounts of moisture when they are melt processed in  
30 conventional equipment. Consequently, polyesters are  
usually carefully dried to very low moisture levels in a  
drier prior to melt processing. The drying process may  
also remove some objectional volatile materials other  
than water.

- 2 -

During the preparation or processing of polyesters such as poly(ethylene terephthalate) (PET) certain byproducts are formed in the melt phase. One such byproduct is acetaldehyde, and its presence in molded 5 objects such as food containers, beverage bottles, water bottles, and the like is quite deleterious from a taste standpoint. Particularly for sensitive beverages such as cola, beer, and water, it is highly desirable to produce container preforms for blow molding processes 10 having less than about 10 ppm of acetaldehyde. Achieving this low level of acetaldehyde is difficult, however, because, as is well known to practitioners of the art, acetaldehyde is continually formed as a byproduct during the polymerization and subsequent melt 15 processing of PET and similar polymers.

Before the discovery of the present invention, therefore, a four-stage process has been universally practiced to provide polyester polymers suitable for uses in which it is important to minimize the presence 20 of acetaldehyde. Such a process typically involves the preparation of a relatively low molecular weight precursor polymer, having an I.V. value of about 0.3-0.6, by melt-phase polymerization techniques that are well known in the art. The acetaldehyde content of such 25 a precursor may range from about 30 ppm to over 150 ppm, depending on the reaction conditions chosen. This precursor is then cooled, shaped into pellets, crystallized, and subjected to further solid-state 30 polymerization at a lower temperature. Typically, a gas is used to strip glycols, acetaldehyde, and other reaction byproducts from the pellets so that at the end of the solid-state process, the I.V. value has been increased to about 0.75 or more, and the acetaldehyde content has been reduced to below about 1 ppm or less.

35 After solid stating, polyesters are commonly

handled and stored in ambient air from which it absorbs moisture. Thus, as a third step, the polymer is usually dried immediately prior to reheating, melting and forming into a useful shape, such as a beverage bottle 5 preform. The processing typically causes a small decrease in the I.V. of the polymer and an increase in acetaldehyde content of from less than 1 ppm in the pellets, to up to about 8 or 10 ppm or more in the shaped article. This dramatic increase in acetaldehyde 10 occurs despite the fact that the molding process takes typically less than one or two minutes to complete.

U.S. Patent Nos. U.S. 5,266,413, U.S. 5,258,233 and U.S. 4,8837,115 disclose various polyamides which are useful in reducing the acetaldehyde levels in PET. U.S. 15 Application Serial No. 595,460, filed February 5, 1996 discloses novel polyesteramide compositions which reduce the levels of acetaldehyde in PET.

Japan Patent Application Sho 62-182065 (1987) discloses blending nylon 6 and other aliphatic 20 polyamides into PET to reduce the acetaldehyde levels below 10ppm when residence times in the melt are kept below 60 seconds.

Several other compounds have also been disclosed to be useful in reducing acetaldehyde. These include 25 ethylenediaminetetraacetic acid (U.S. 4,357,461), alkoxylated polyol (U.S. 5,250,333), bis(4- $\beta$ -hydroxyethoxyphenyl) sulfone (U.S. 4,330,661), zeolite compounds (U.S. 5,104,965), 5-hydroxyisophthalic acid (U.S. 4,093,593), poly(ethylene isophthalate) 30 (U.S. 4,403,090) and supercritical carbon dioxide (U.S. 5,049,647 and U.S. 4,764,323) and protonic acid catalysts (U.S. 4,447,595 and U.S. 4,424,337).

U.S. 4,361,681 discloses that the capping of 35 hydroxyl end groups of PET with anhydrides such as succinic or phthalic acid anhydride will suppress

- 4 -

acetaldehyde formation. U.S. 5,243,020 discloses pyromellitic dianhydride for end capping of PET.

U.S. 4,356,299 discloses that the use of catalysts based on low levels of Ti and Sb are beneficial in 5 limiting the amount of acetaldehyde formed.

U.S. 5,656,719 discloses the production of molded polyesters articles having low acetaldehyde via melt polymerization and a post condensation reactor. The post condensation reactor is operated at low vacuum 10 levels and significant residence times to build up inherent viscosity.

U.S. 5,656,221 discloses the production of molded polyesters articles having low acetaldehyde via addition of an acetaldehyde reducing additive and molding 15 directly from melt polymerization. Cobalt compounds in addition to conventional polymerization catalysts are required in amounts from 5 to 120 ppm.

Integrated processes which produce PET articles with low acetaldehyde but do not disclose the addition 20 of acetaldehyde reducing additives have also been disclosed. U.S. Application Serial No. 609,197 describes a process for direct molding of polyester from the melt. U.S. Application Serial No. 498,404 discloses a process and apparatus for distributing molten PET to a 25 multiplicity of molding machines. U.S. 5,648,032 describes processes for making low acetaldehyde poly(ethylene terephthalate) articles without using solid stated polymer.

Several patents disclose the use of vented 30 extruders to devolatilize polymers. U.S. 5,597,891 discloses a process for producing reduced acetaldehyde polyester articles by using a purge gas in a vented extruder to remove acetaldehyde. U.S. 5,102,594 discloses thermoplastic condensation polymer supplied to 35 extruder in powder form to a vented extruder). U.S.

- 5 -

3,486,864 discloses using a vacuum to remove volatile glycol products from a remelted prepolymer as fast as possible. U.S. 3,913,796 discloses using an extrusion screw for heating the solid resin to a semi-molten state 5 and U.S. 4,060,226 disclose excluding oxygen by means of a check valve.

Brief Description of the Drawing

Figure 1 is a flow diagram showing several 10 potential embodiments of the process of the present invention.

Summary of the Present Invention

The present invention includes a process whereby 15 low acetaldehyde polyesters such as PET and similar polymers may be prepared and used without need for the solid stating process nor the usual drying of solid pellets. Surprisingly the present invention is accomplished without the need for Co compound catalysts 20 or a post condensation reactor.

Specifically the present invention includes a process for producing molded articles comprising the steps of:

- a) melt reacting at least one glycol and at least 25 one dicarboxylic acid to form a polyester having an I.V. of at least about 0.5 dL/g, wherein said at least one glycol is selected from the group consisting of glycols having up to 10 carbon atoms and mixtures thereof and said dicarboxylic is selected from the group consisting of alkyl dicarboxylic acids having 30 2 to 16 carbon atoms, aryl dicarboxylic acids having 8 to 16 carbon atoms and mixtures thereof in the presence of a catalyst which is substantially free from Co compounds;

- 6 -

- b) adding an acetaldehyde reducing additive to said polyester to form a reduced acetaldehyde polyester; and
- c) forming said reduced acetaldehyde polyester into shaped articles directly from step b.

5 Additionally several optional steps such as melt devolatilizing, pelletizing, storing, transporting, remelting, and drying, may be included to fit the needs of a specific process. If the polymer is pelletized the 10 acetaldehyde reducing additive may be added prior to pelletization or after remelting. The shaped articles made from the process of the present invention display surprisingly low acetaldehyde content.

15 Description of the Invention

As used herein the term "I.V." refers to the Inherent Viscosity of the polymer, as determined on a solution of 0.5 gm of polymer dissolved in 100 ml of a mixture of phenol (60% by volume) and tetrachloroethane (40% by volume).

20 The present invention provides a process to make shaped articles from polymers which display both high molecular weight and low acetaldehyde content without requiring the use of solid-state polymerization, solid-state devolatilization or a post condensation reactor.

25 Specifically, a preferred embodiment of the process of the present invention provides an improved "melt-to-mold" process in which polyester polymers or copolymers are prepared in the melt phase to an I.V. value of greater than about 0.5 dL/g; an acetaldehyde reducing additive is added to the polymer melt and then the melt is fed directly from the polycondensation reactor to at least one molding or shaping machine. No intervening 30 post condensation or I.V. build up is required.

- 7 -

Any conventional melt polymerization process capable of producing the required I.V. may be used for the polycondensation and the reactor may comprise one or more reaction vessels or zones which are capable of producing polyester having the required I.V.

5 Preferably the I.V. is at least about 0.65 dL/g so the polymer directly from the melt has sufficient molecular weight to provide high performance molded articles such as containers. In the present invention, 10 the desired I.V. is generated in the polycondensation reaction and no post condensation reactor is necessary.

Generally the melt polymerization is conducted under conditions which are known in the art, however, for the present invention Co compounds are not added.

15 The AA reducing additive may be any additive known to reduce AA. Suitable additives include polyamides such as those disclosed in U.S. Patent Nos. U.S. 5,266,413, U.S. 5,258,233 and U.S. 4,8837,115; polyesteramides such as those disclosed in 20 U.S. Application Serial No. 595,460, filed February 5, 1996; nylon-6 and other aliphatic polyamides such as those disclosed in Japan Patent Application Sho 62-182065 (1987); ethylenediaminetetraacetic acid (U.S. 4,357,461), alkoxylated polyols (U.S. 5,250,333), 25 bis(4- $\beta$ -hydroxyethoxyphenyl)sulfone (U.S. 4,330,661), zeolite compounds (U.S. 5,104,965), 5-hydroxyisophthalic acid (U.S. 4,093,593), poly(ethylene isophthalate) (U.S. 4,403,090), supercritical carbon dioxide (U.S. 5,049,647 and U.S. 4,764,323) and protonic acid 30 catalysts (U.S. 4,447,595 and U.S. 4,424,337).

35 Preferably the AA reducing additive is selected from polyamides, polyesteramides and poly(ethylene isophthalate). Suitable polyamides include homo and copolyamides with AB or A<sub>2</sub>B<sub>2</sub> structures such as poly(caprolactam), poly(hexamethylene-adipamide),

- 8 -

poly(m-xylylene-adipamide), etc. Branched or hyperbranched polyamides can also be used.

Suitable poyesteramides include the polyesteramides prepared from terephthalic acid, 1,4-cyclohexane-5 dimethanol, isophthalic acid and hexamethylene diamine (preferably with about 50:50 ratio of the diacids and a 50:50 ratio of the glycol to the diamine); the polyesteramide prepared from terephthalic acid, 1,4-cyclohexanedimethanol, adipic acid and hexamethylene diamine; the polyesteramides prepared from terephthalic acid, 1,4-cylcohexanedimethanol and bis(p-amino-cylcohexy)methane. Other known scavengers such as polyethyleneimine may also be used.

The AA reducing additive is generally added in an amount between about 0.1 and 5 weight %. More preferably between about 0.2 and 3 weight % additive is added. It should be understood that the additive may be added individually or as a concentrate in a compatible polymer base resin.

Devolatilization of the polymer may also be used in conjunction with the AA reducing additive to further remove acetaldehyde and other undesirable volatiles which are generated. The devolatilization step may be conducted in a separate devolatilization unit, concurrently in the polycondensation reactor, or concurrently in molding machine.

The devolatilization device can be any apparatus known in the art for generating a large amount of surface area per unit volume and\or for rapidly regenerating the exposed melt surface. The devolatilization device should subject the liquid surface to a low partial pressure of acetaldehyde either by inert gas purging as described in U.S. 5,597,891, applied vacuum or both. The devolatilization apparatus may be a vented single-screw extruder (U.S. 4,107,787),

- 9 -

a vented twin-screw extruder (U.S. 3,619,145), a rotating disk processor (U.S. 4,362,852), or device which generates thin strands of polymer (U.S. 3,044,993), all of which are incorporated herein by reference. The devolatilization step of the present invention is conducted at pressures which are greater than about 25mm Hg, and preferably less than or near atmospheric pressures. Residence times should be short enough to insure that substantial increases in I.V. are not encountered. For the purposes of this invention a substantial increase in I.V. is an increase greater than about 0.1 dl/g, preferably greater than about 0.05 dl/g and more preferably greater than about 0.03 dl/g.

Several additional optional steps may also be added to the process of the present invention. These steps include: melt devolatilization, pelletizing, storage and transportation, remelting and drying. It should be appreciated that the optional steps may be used alone (i.e. devolatilization) or in combination with each other (pelletizing and remelting, or storage, transportation and remelting, etc.). Suitable combinations of the optional steps are well known in the art and need not be individually detailed here.

Figure 1 illustrates many possible combinations of the operations in going from a high molecular weight melt phase polymer to molded articles. A preferred combination of operations is illustrated in Figure 1 as the Path G and would be to prepare the polymer in the melt to the desired I.V., add the additives and form the improved polymer melt into useful shaped articles, such as for example beverage bottle preforms, said shaped articles having surprisingly low acetaldehyde content.

A second combination of operations illustrated in Figure 1 as Path N would be to prepare the polymer in the melt to the desired I.V., devolatilize the melt to

- 10 -

lower the acetaldehyde somewhat and add the AA reducing additive to further reduce the acetaldehyde and then form the improved polymer melt into useful shaped articles. The other paths illustrated in Figure 1 show 5 other combinations of operations all of which lead to the desired end of having formed articles containing desirably low acetaldehyde levels starting from melt-phase, high molecular weight polymer and without having to solid-state polymerize the polymer. Not only does the 10 process of the present invention avoid the costly additional steps of the conventional process of solid-state polymerization, but the shaped articles produced thereby possess both low AA content and other superior properties such as, for example, less loss of molecular 15 weight due to breakdown, and freedom from defects known as "bubbles" and "unmelts" which are sometimes formed during the molding of solid stated materials from the conventional process.

The molding or shaping device may be any of those 20 generally known in the art. For example, injection molds may be used to form preforms used to blow bottles, food/beverage containers, trays, or other desirable shapes. Also the polymer melts may be used in extrusion blow molding operations to provide bottles, food 25 containers, and the like. The polymer melt may similarly be fed to an extruder to produce films, sheet, profiles, pipe and the like.

The combinations of operations illustrated in 30 Figure 1 is not intended to be limiting because it is obvious that other operations might be added and the sequence of some operations might be changed and still achieve the same ends.

If the pelletization of the polymer is desired as 35 an intermediate process, then one must deal with any moisture absorbed by the polymer. Polyesters are well

- 11 -

known by those who practice the art to be degraded by moisture present during conventional melt processing. The usual method of removing the moisture is to crystallize the polymer to minimize sticking of the 5 pellets to each other and then to hold it at a temperature high enough to remove the vaporized moisture. In order to have a more economical process, either one or a combination of both of the following methods may be used to provide a molten polymer free 10 from degradation by moisture. The polyester is often extruded into a water bath to cool it so cutters can chop it in to pellets. One may use a dewatering process immediately following the chopping to completely remove the surface moisture prior to transferring the polymer 15 to storage. Such dewatering equipment is sold, for example, by Gala Industries, Inc. of Eagle Rock, Virginia. When the storage facility is blanketed or purged with a dry gas, the polymer will remain dry until use. Because the polymer is kept dry, there is no need 20 for crystallization or drying. If the polymer is not kept dry so that it is amorphous and contains moisture, it may be fed to an extruder in which the melting zone is either purged with a gas or subjected to a vacuum. As the polymer heats and begins to melt, the high vapor 25 pressure of the water causes it to separate into the vapor space. To minimize problems caused by foaming, it is preferred to use a machine that removes much of the moisture through an ambient pressure purge of the melting zone followed by a short residence time vacuum 30 devolatilization in a second zone which is isolated by melt dams caused by the design and operation of the extruder as is commonly done by those skilled in the polymer extrusion art.

During the melt drying, some other volatile 35 materials will be removed in addition to removing water.

- 12 -

However, because of the low levels of acetaldehyde desired for articles to be used in contact with food, usually additional devolatilization steps or the additives to reduce acetaldehyde will be desired to 5 produce a polymer melt of the desired quality.

In some cases it may be desirable to remove part of the acetaldehyde by a devolatilization process as illustrated in Paths K-N. Acetaldehyde can be readily removed from the molten polymer in the extruder or gear 10 pump equipment by purging it with a gas or by subjecting the melt to conditions of vacuum. Typical acetaldehyde levels in polymer coming from the final reactor before this treatment are generally in the range of about 30-300 ppm for polyester of I.V.=0.4-0.65 made by any of 15 the known processes, followed by polymer filtration to remove gels and particulate matter, followed by another polycondensation reactor to produce high-viscosity polyesters of I.V. > 0.68. The melt may be devolatilized, have additives mixed and used directly or 20 it may be pelletized for later use. After the polymer is pelletized it will be an amorphous material containing the acetaldehyde that was in the melt. After remelting with drying, most of that acetaldehyde will remain to be removed by the use of additives and further 25 devolatilization.

Suitable melt processing temperatures for poly(ethylene terephthalate) polymers will generally be in the range of about 260 to about 310°C. In the cases where polymer is never solidified, the melt temperatures 30 can be kept toward the lower end of the range. The lower temperature is well known to assist in reducing acetaldehyde. One advantage of the present process is that because the pellets of polymer are amorphous, they may be processed at somewhat lower temperatures than is 35 commonly used to melt solid stated crystalline pellets.

- 13 -

Of course, processing temperatures may be adjusted for other types of polyesters depending on the melting point, I.V. value and the like.

5 The process of the present invention is less expensive to operate than making crystalline, solid-stated polymer, provides energy savings and lower capital requirements over conventional processes, and produces parisons and molded objects with better clarity, significantly fewer or no unmelts or other 10 defects and lower concentrations of undesirable byproducts.

15 Polymers that are particularly useful in this process include poly(ethylene terephthalate), poly(ethylene naphthalenedicarboxylate), and copolyesters containing up to about 50 mole% of 20 modifying dibasic acids and/or glycols. Modifying dibasic acids may contain from about 2 to about 40 carbon atoms and include isophthalic, adipic, glutaric, azelaic, sebacic, fumaric, dimer, *cis*- or *trans*-1,4-cyclohexanedicarboxylic, the various isomers of naphthalenedicarboxylic acids and the like. More 25 preferably the polyesters of the present invention contain at least about 80 mole% terephthalic acid, naphthalenedicarboxylic acid or a mixture thereof.

30 Highly useful naphthalene dicarboxylic acids include the 2,6-, 1,4-, 1,5-, or 2,7- isomers but the 1,2-, 1,3-, 1,6-, 1,7-, 1,8-, 2,3-, 2,4-, 2,5-, and/or 2,8-isomers may also be used. The dibasic acids may be used in acid form or as their esters such as the dimethyl esters for example.

35 Typical modifying glycols may contain from about 3 to about 10 carbon atoms and include propylene glycol, 1,3-propanediol, 1,4-butanediol, 1,6-hexanediol, diethylene glycol, 1,4-cyclohexanediol, 1,4-cyclohexanedimethanol, and the like. The

- 14 -

1,4-cyclohexanedimethanol may be in the *cis* or the *trans* form or as *cis/trans* mixtures. More preferably the polyesters of the present invention comprise at least about 80 mole % ethylene glycol.

5       Particularly preferred polyesters comprise terephthalic acid and a mixture of about 60 to about 99 mole % ethylene glycol and about 40 to about 1 mole % cyclohexanedimethanol.

10      Generally the polyesters produced in the first step of the present invention have I.V.'s which are at least about 0.5 dL/g, more preferably at least about 0.65 dL/g and most preferably between about 0.65 and about 0.85 dL/g.

15      The polyesters of this invention are readily prepared using polycondensation reaction conditions well known in the art. Typical polyesterification catalysts which may be used include titanium alkoxides, dibutyl tin dilaurate, and antimony oxide or antimony triacetate, used separately or in combination, 20     optionally with zinc, manganese, or magnesium acetates or benzoates and/or other such catalyst materials as are well known to those skilled in the art. Phosphorus compounds and toners as disclosed in U.S. 5,384,377 and U.S. 5,372,864, which is incorporated herein by 25     reference may also optionally be present. Although we prefer to use continuous polycondensation reactors, batch reactors operated in series may also be used.

30      Although we prefer to use the polyesters in this process in an unmodified form, other components such as nucleating agents, branching agents, colorants, pigments, fillers, antioxidants, ultraviolet light and heat stabilizers, impact modifiers and the like may be used if desired.

- 15 -

Examples

Determination of acetaldehyde concentration in polyethylene terephthalate (PET)

PET samples were dried and extruded as described in 5 the example below, and collected on dry ice to quench the melt. The polymer was immediately chopped into pellets and stored at -40°C for no longer than 2 days prior to AA analysis. The stored samples were ground in a Wiley mill to pass a 20 mesh screen. For the analysis 10 a 0.5 g sample was placed into a sample tube that was immediately sealed. The sample was analyzed by dynamic headspace gas chromatographic analysis using a Hewlett-Packard 5890 Gas Chromatograph with a Perkin Elmer Automatic Thermal Desorption ATD-50 as the injection 15 system. Acetaldehyde was desorbed by heating the sample at 150°C for ten minutes. A standard PET level was established by grinding the extruded PET and subjecting it to the same test.

20 I.V.

I.V. was measured by standard methods at 25°C at a concentration of 5 g/L in a phenol/tetrachlorethane solution (60/40 wt/wt).

25 Composition used

The PET used in the examples is a copolyester consisting of 100 mole percent of terephthalic acid, 98 to 99 mole percent ethylene glycol and 1 to 2 mol percent 1,4-cyclohexanedimethanol, having an I.V. of 30 about 0.74. The PET was pelletized prior to feeding it to a vented twin-screw extruder.

Simulated high AA samples were produced as follows: Granulated PET was placed in a container and an appropriate amount of liquid acetaldehyde was added. 35 The container was sealed and the contents were allowed

- 16 -

to equilibrate at room temperature for 1 day before use in the additive experiments.

The PET/additive blends were prepared by batch-wise dry mixing in a bag prior to feeding into the extruder.

5 The additives where added at the level shown in Table 1.

Additive 1 is a high molecular weight (Mw=38,200) polyesteramide prepared from terephthalic acid, cyclohexanedimethanol, and hexamethylene diamine with a 50/50 molar ratio of the diol and diamine.

10 Additive 2 is a low molecular weight (Mw=17,800) polyesteramide prepared from terephthalic acid, cyclohexanedimethanol, and hexamethylene diamine with a 50/50 molar ratio of the diol and diamine.

15 Additive 3 is a polyamide prepared from adipic acid and m-xylynediamine.

Examples 1-12

The polymer/additive compositions shown in Table 1, below were fed to a vented twin screw extruder in a metered fashion. The extruder screw RPMs were maintained at 30. Zone 1 of the extruder, following the water-cooled feed zone, was set to 265°C. Zones 2 and 3, the heated extruder vented area, were controlled at 272.5°C. The final zone, Zone 4, was between the vent and the discharge port and was kept at 260°C. For gas sweep examples, nitrogen preheated to 285°C was used and was fed through the extruder vent so as to sweep over the polymer melt. The gas flow was controlled at 250 sccm by a mass flow controller and vented to atmospheric pressure through a bubble trap. The non-swept examples had the gas flow turned off, but were still allowed to vent to atmospheric pressure via the bubble trap. The residence time of the molten polymer in the extruder after venting was 3 minutes. Examples 1-12 in Table 1 are the examples of this invention demonstrating the exceptional acetaldehyde reducing capability of the

- 17 -

various additives in this extrusion process. For each of these examples, the extruded polymer was formed into rods.

- 18 -

Table 1. Examples of the Effect of Additives on AA Levels

| Ex # | Precsr I.V.<br>(dL/g) | Precsr AA<br>Content<br>(ppm) | Additive     | N <sub>2</sub> sweep<br>(sccm) | Extrdte<br>AA<br>(ppm) | Extrdte<br>I.V.<br>(dL/g) |
|------|-----------------------|-------------------------------|--------------|--------------------------------|------------------------|---------------------------|
| 1    | 0.74                  | 2                             | none         | 0                              | 4.9                    | 0.61                      |
| 2    | 0.74                  | 2                             | none         | 250                            | 2.7                    | 0.7                       |
| 3    | 0.74                  | 2                             | A1 (1 wt%)   | 0                              | 1.7                    | 0.62                      |
| 4    | 0.74                  | 2                             | A1 (1 wt%)   | 250                            | 0.5                    | 0.68                      |
| 5    | 0.74                  | 176                           | none         | 0                              | 52                     | 0.64                      |
| 6    | 0.74                  | 176                           | none         | 250                            | 10                     | 0.73                      |
| 7    | 0.74                  | 176                           | A1 (1 wt%)   | 0                              | 18                     | 0.63                      |
| 8    | 0.74                  | 176                           | A1 (1 wt%)   | 250                            | 1                      | 0.7                       |
| 9    | 0.74                  | 176                           | A2 (1 wt%)   | 0                              | 26                     | 0.66                      |
| 10   | 0.74                  | 176                           | A2 (1 wt%)   | 250                            | 1.6                    | 0.7                       |
| 11   | 0.74                  | 176                           | A3 (0.5 wt%) | 0                              | 14                     | 0.64                      |
| 12   | 0.74                  | 176                           | A3 (0.5 wt%) | 250                            | 1.4                    | 0.72                      |

- 19 -

Significantly lower AA levels were achieved when an additive was used in combination with a nitrogen sweep. Residence time (not shown) in the extruder was sufficient to achieve a significant increase in I.V. 5 (0.04-0.09) compared to controls when using a nitrogen purge. The I.V. increase is due to a lowering of the ethylene glycol partial pressure, resulting in further polycondensation and a higher molecular weight of the polymer.

- 20 -

WE CLAIM

1. A process comprising the steps of:
  - a) melt reacting, in the presence of a catalyst which is substantially free of Co compounds, at least one glycol and at least one dicarboxylic acid to form a polyester having an I.V. of at least about 0.5 dL/g, wherein said at least one glycol is selected from the group consisting of glycols having up to 10 carbon atoms and mixtures thereof and said dicarboxylic is selected from the group consisting of alkyl dicarboxylic acids having 2 to 16 carbon atoms, aryl dicarboxylic acids having 8 to 16 carbon atoms and mixtures thereof;
  - b) adding an acetaldehyde reducing additive to said polyester to form a reduced acetaldehyde polyester; and
  - c) forming said reduced acetaldehyde polyester into articles directly from step b.
2. The process of claim 1 further comprising the step of devolatilizing said polyester to remove acetaldehyde prior to said forming step (c).
3. The process of claim 1 wherein said polyester from step a has an I.V. of at least about 0.65 dL/g.
4. The process of claim 1 wherein said polyester from step a has an I.V. between about 0.65 and about 0.85 dL/g.
5. The process according to claim 1 wherein said dicarboxylic acid comprises at least about 80% mole terephthalic acid.
6. The process of claim 1 wherein said dicarboxylic acid comprises at least about 80% mole naphthalenedicarboxylic acid.

- 21 -

7. The process of claim 1 wherein said glycol comprises at least 80 mole% ethylene glycol.

8. The process of claim 1 wherein said glycol is a mixture of ethylene glycol and cyclohexanedimethanol.

5 9. The process of claim 1 wherein said acetaldehyde reducing additive is selected from the group consisting of polyamides, polyesteramides, nylon-6, aliphatic polyamides, ethylenediaminetetraacetic acid, alkoxylated polyols, bis(4-β-10 hydroxyethoxyphenyl)sulfone, zeolite compounds, 5-hydroxyisophthalic acid, poly(ethylene isophthalate), supercritical carbon dioxide, protonic acid catalysts and mixtures thereof.

15 10. The process of claim 1 wherein said acetaldehyde reducing additive is selected from the group consisting of polyamides, polyesteramides and poly(ethylene isophthalate).

20 11. The process of claim 10 wherein said polyamides are selected from the group consisting of homo and copolyamides with AB or A<sub>2</sub>B<sub>2</sub> structures.

25 12. The process of claim 11 wherein said polyamides are selected from the group consisting of poly(caprolactam), poly(hexamethylene-adipamide), poly(m-xylylene-adipamide) and mixtures thereof.

30 13. The process of claim 11 wherein said polyesteramides are selected from the group consisting of polyethyleneimine, polyesteramides prepared from terephthalic acid, 1,4-cyclohexanedimethanol, isophthalic acid and hexamethylene diamine; the polyesteramide prepared from terephthalic acid, 1,4-cyclohexanedimethanol, adipic acid and hexamethylene diamine; the polyesteramides prepared from terephthalic acid, 1,4-cyclohexanedimethanol and bis(p-aminocyclohexyl)methane and mixtures thereof.

- 22 -

14. The process of claim 1 wherein said acetaldehyde reducing additive is added in an amount between about 0.1 and 5 weight %.

5 15. The process of claim 1 wherein said acetaldehyde reducing additive is added in an amount between about 0.2 and 3 weight % additive is added.

10 16. The process of claim 1 wherein said dicarboxylic acid comprises terephthalic acid and said glycol is a mixture of about 60 to about 99 mol% ethylene glycol and about 40 to about 1 mol% cyclohexanedimethanol.

17. The process of claim 2 wherein reacting and devolatilizing steps are conducted in a single piece of equipment.

15 18. The process of claim 1 wherein said acetaldehyde reducing additive is added to said polyester individually.

20 19. The process of claim 1 wherein said acetaldehyde reducing additive is added to said polyester as part of a concentrate.

20 20. The process of claim 1 wherein at least one toner is added to said melt reacting step a).

25 21. The process of claim 2 wherein said devolatilizing is conducted at pressures which are greater than about 25mm Hg.

22. The process of claim 2 wherein said devolatilizing is conducted at pressures which are near or at atmospheric pressures.

30 23. The process of claim 2 wherein said devolatilizing is conducted at residence times short enough to insure that a substantial increase in I.V. is not achieved.

24. The process of claim 23 wherein said substantial increase is greater than about 0.1 dl/g.

- 23 -

25. The process of claim 23 wherein said substantial increase is greater than about 0.05 dl/g.

26. The process of claim 23 wherein said substantial increase is greater than about 0.03 dl/g.

5 27. The process of claim 1 wherein said polyester has an acetaldehyde content of less than about 10 ppm.

28. An article which is formed according to the process of claim 1 selected from the group comprising molded, shaped and extruded articles.

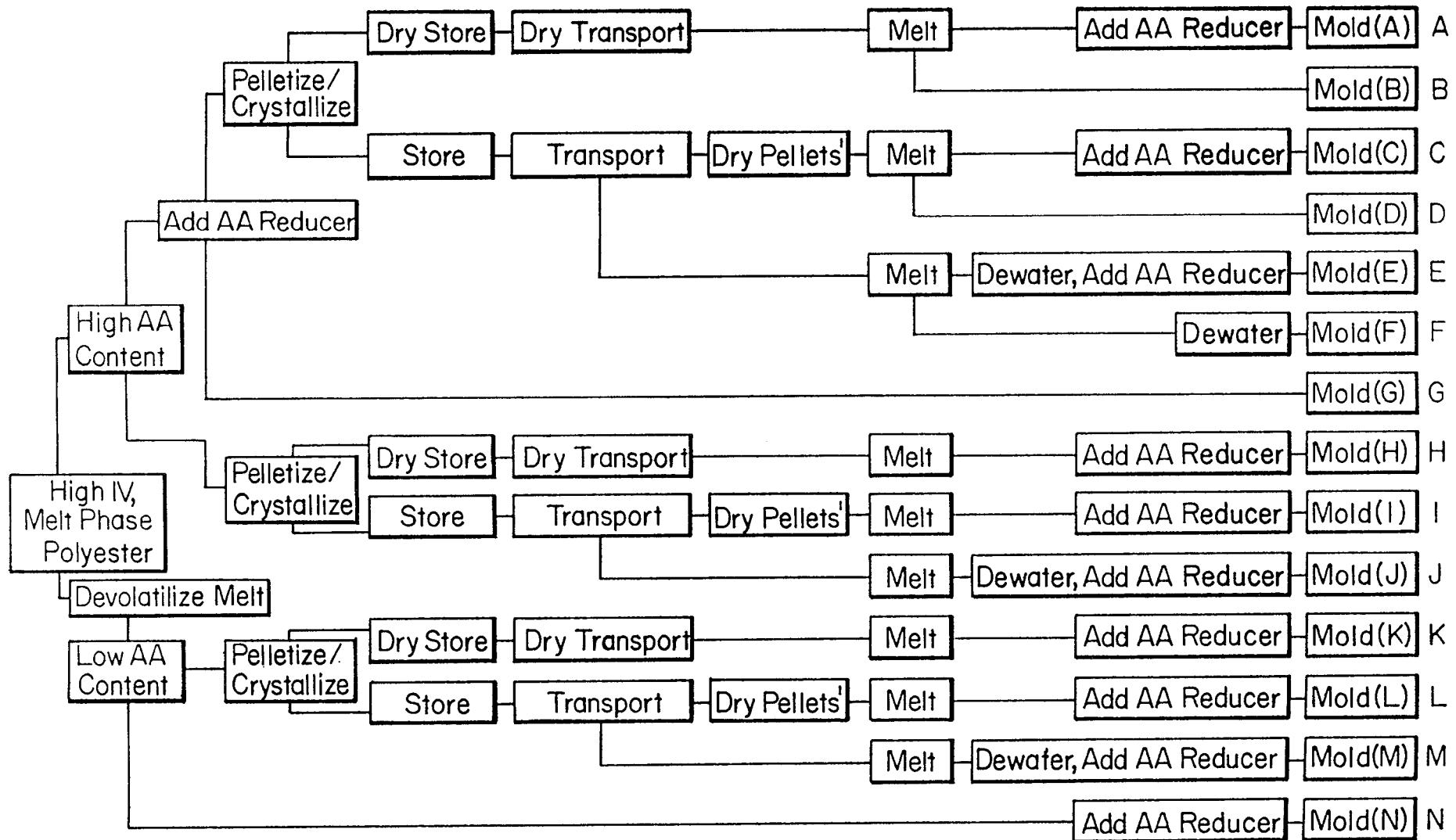


Fig. 1

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 97/19403

## A. CLASSIFICATION OF SUBJECT MATTER

## IPC6: C08G 63/88

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)

## IPC6: C08G

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 practicable, search terms used)

## WPI, CAPLUS

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages        | Relevant to claim No. |
|-----------|---|-----------------------|
| P, X      | WO 9731968 A1 (EASTMAN CHEMICAL COMPANY),<br>4 Sept 1997 (04.09.97), See the claims<br>-- | 1-28                  |
| P, Y      | WO 9705186 A1 (EASTMAN CHEMICAL COMPANY),<br>13 February 1997 (13.02.97), abstract<br>--  | 1-28                  |
| Y         | DE 19503053 A1 (ZIMMER AG), 8 August 1996<br>(08.08.96), abstract<br>--                   | 1-28                  |
| Y         | US 4356299 A (MICHAEL S. CHOLOD ET AL),<br>26 October 1982 (26.10.82), abstract<br>--     | 1-28                  |

 Further documents are listed in the continuation of Box C. See patent family 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

19 February 1998

04.03.98

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

MONIKA BOHLIN

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 97/19403

| C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT |   |                       |
|---|---|-----------------------|
| Category*   | Citation of document, with indication, where appropriate, of the relevant passages      | Relevant to claim No. |
| A   | US 4675378 A (JOHN D. GIBBON ET AL), 23 June 1987<br>(23.06.87), claims 1,2,12,13<br>-- | 1-28                  |
| A   | EP 0717061 A2 (SINCO ENGINEERING S.P.A.),<br>19 June 1996 (19.06.96)<br>--<br>-----     | 1-28                  |

# INTERNATIONAL SEARCH REPORT

Information on patent family members

03/02/98

International application No.

PCT/US 97/19403

| Patent document cited in search report | Publication date | Patent family member(s) |            | Publication date |
|--|------------------|-------------------------|------------|------------------|
| WO 9731968 A1                          | 04/09/97         | AU                      | 1977797 A  | 16/09/97         |
| WO 9705186 A1                          | 13/02/97         | AU                      | 6642596 A  | 26/02/97         |
|  |                  | US                      | 5648032 A  | 15/07/97         |
| DE 19503053 A1                         | 08/08/96         | US                      | 5656221 A  | 12/08/97         |
| US 4356299 A                           | 26/10/82         | EP                      | 0091180 A  | 12/10/83         |
|  |                  | JP                      | 58189227 A | 04/11/83         |
| US 4675378 A                           | 23/06/87         | NONE                    |            |                  |
| EP 0717061 A2                          | 19/06/96         | AU                      | 679398 B   | 26/06/97         |
|  |                  | AU                      | 3910495 A  | 27/06/96         |
|  |                  | CA                      | 2163954 A  | 17/06/96         |
|  |                  | CN                      | 1130644 A  | 11/09/96         |
|  |                  | IT                      | 1271293 B  | 27/05/97         |
|  |                  | IT                      | MI942544 A | 16/03/95         |
|  |                  | JP                      | 8231700 A  | 10/09/96         |
|  |                  | PL                      | 311792 A   | 24/06/96         |
|  |                  | US                      | 5708124 A  | 13/01/98         |