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3,405,154

STABILIZATION OF ALUMINUM ALKOXIDES
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ABSTRACT OF THE DISCLOSURE

Aluminum trialkoxides are stabilized against pyrolysis by adding a small amount of a low-molecular-weight aluminum alkyl, an alkali metal or an aluminum hydride.

This invention relates to stabilization of aluminum alkoxides as obtained by Ziegler growth of aluminum alkyls followed by oxidation. In one aspect, this invention relates to stabilizing such growth product against thermal degradation. In another aspect, this invention relates to a reduction of nonalcoholic impurities in oxidized growth product.

For several years now, it has been known that aluminum alkyls can be reacted with low molecular weight 1-olefins, particularly ethylene, to form aluminum alkyls wherein the resulting aluminum alkyls contain alkyls of greater chain length than did the original aluminum compound. Most generally aluminum triethyl or aluminum tripropyl will be the starting aluminum compound, depending upon whether even- or odd number chain lengths are desired. It is also known to oxidize the aluminum alkyl growth product to the alkoxide and to hydrolyze the resulting alkoxide, usually with H_2SO_4 , to produce long chain alcohols and aluminum sulfate. The resulting primary alcohols generally will contain 8 to 20 carbon atoms or more.

Typically, the oxidized growth product will contain esters, ethers and carbonyl compounds. However, some of the higher boiling impurities will remain with the aluminum growth product.

We have found that aluminum alkoxides produced by the oxidation of this growth process are not as stable against pyrolysis as are the pure alkoxides. While the reason for this lack of thermal stability is not completely known to us, it is believed that the presence of these impurities contribute to the formation of additional impurities. It is also known that during the oxidation process some side reactions take place forming such impurities. The alkoxides, after formation, are stripped to remove such impurities. It is during this stripping process additional impurities are formed by pyrolysis at the expense of primary alcohol production. One such stripping method is disclosed in U.S. Patent 3,104,251.

It is an object of this invention to stabilize alkoxides containing growth product and oxidation product impurities against pyrolysis.

In one aspect, an object of this invention is to stabilize growth product against degradation during oxidation and stabilizing the resulting alkoxide against pyrolysis.

Other objects of this invention will be apparent to those skilled in the art, having been given this disclosure and the attached claims.

According to this invention, aluminum alkoxides obtained by the growth product, followed by oxidation, and having an average carbon content in the alkyl portion of said alkoxide of at least 8 is stabilized against pyrolysis by the addition of an aluminum trialkyl or a metal hydride such as an aluminum alkyl hydride or an alkali metal hydride, and wherein the alkyl groups of the aluminum alkyl contain 2 to 4 carbon atoms.

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According to one embodiment of this invention, the aluminum alkoxide is stabilized after oxidation by any of the foregoing classes of compounds.

Typical stabilizers, therefore, include aluminum triethyl, aluminum triisopropyl, aluminum tributyl, aluminum hydride, aluminum diethyl hydride, aluminum propyl dihydride, sodium hydride and the like.

Typical systems would include the growth product and any of the hydrides mentioned above and alkoxides, obtained by oxidation of growth product, containing any of the compounds listed above.

The amount of stabilizer used will vary with the particular stabilizer; however, in general 2 to 7 weight percent, based on the aluminum compound being stabilized, is used. With aluminum trialkyls of higher molecular weight than aluminum triethyl, a larger amount is generally required than is required for the aluminum triethyl. Also, the hydrides are useful in lower percentages than are the aluminum trialkyls for equivalent control.

In one typical process, aluminum triethyl is reacted with ethylene to produce aluminum trialkyls having a typical Poisson distribution of alkyl chains. The unreacted ethylene and low boiling side products are flashed off. The product trialkyl is then oxidized at atmospheric pressure and temperature by passing air through the aluminum trialkyl product forming the corresponding aluminum trialkoxides and side reaction products including esters, ethers, aldehydes and the like. About 2 percent by weight aluminum triethyl is added to the resulting alkoxides, and the alkoxides are stripped by volatilization to remove these side reaction products. After stripping, the alkoxides are considerably purer than when the aluminum triethyl is not used, and the total yield is improved. The alkoxides can then be hydrolyzed with H_2SO_4 to produce alcohols corresponding to the alkoxides and aluminum sulfate. The alcohols are then fractionally distilled to close boiling fractions.

We have found in some cases that the addition of the stabilizer is advantageously added during the oxidation of the growth product, preferably after the oxidation approaches 80 to 90 percent completion. By such addition, we find that we attain somewhat higher yields of the desired product, e.g., reduce formation of impurities than if we add the stabilizer at the end of the oxidation.

We have found that the oxidized growth product undergoes reactions, when heated to a moderate temperature to form branched, unsaturated alcohols. These reactions are completed in a few minutes at $150^\circ C$. but require several hours below $100^\circ C$. In the stabilization treatment, addition of the stabilizer must be sufficiently rapid to substantially avoid the dimerization reactions. Thus, it is seen that time will vary with temperature.

We have further found that with the metal hydrides as defined above, that not only is the growth product stabilized against pyrolysis, but the hydrides reduce the amount of impurities initially present.

EXAMPLES

Two runs were made to illustrate the stabilizing effect of the stabilizer of this invention. Due to the impurity content of oxidized growth product and the difficulty encountered in analyzing for these high percentages, a plant-stripped, oxidized growth product is utilized in the examples to illustrate the effectiveness of these stabilizers when the alkoxides are subjected to heat.

Example I

To 164.1 grams of plant-stripped, oxidized growth product were added 3.1 grams of aluminum triethyl. A por-

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tion of this mixture was sealed in a glass ampoule and heated at 310° C. for 1 hour. A control was carried out in the same manner except that the aluminum triethyl was omitted. The analytical results are given below:

Treated Sample:	Control
Ca. 1.3% olefin -----	Ca. 5-6% olefins.
Lesser amounts of ethers	Ca. 20% ethers; lesser
and unknown decom-	amounts of unknown
position products.	decomposition prod-
	ucts.

Example II

In a 2-liter flask with a mechanical stirrer, thermometer and take-off assembly were placed 800 grams of plant-produced aluminum alkoxides. The flask was flushed with argon. As the temperature was increased to 150° C., 35 ml. (28 grams) diethyl aluminum hydride ($H/Al=0.85$) were added. During the initial period of addition, gas was evolved. At the end of the addition, the mixture was nearly colorless. The mixture had no esters as evidenced by infrared analysis.

Solvent was removed by heating to 250° C. under full pump vacuum. The volatile fraction (230 grams) contained no ester or alcohol as evidenced by infrared analysis. The mixture was hydrolyzed with excess 25% H_2SO_4 , washed with water and distilled.

A control run was made as above except no diethyl aluminum hydride was added. The results are given below:

Sample	Stabilized	Unstabilized
Overhead.....	No ester or alcohol present.	3% ester present (calculated as decylacetate; alcohol also present).
Crude alcohol..	Max. 231 m; abs. = .09 at 1:100 dilution.	Max. 229 m; abs. = 0.11 at 1:1000 dilution.
$C_{12}OH$	2% total impurities*	3.4% total impurities.
$C_{14}OH$	3.4% total impurities	4.1% total impurities.
$C_{16}OH$	2.3% total impurities	6.4% total impurities.

*Any component other than straight chain primary alcohol.

Example III

Two runs were made to illustrate the advantage of treating the growth product at a low temperature as follows.

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Run 1. A portion of plant oxidized growth product was treated with aluminum diethyl hydride wherein the temperature was maintained below 50° C. After work up as in Example II, the C_{12} - C_{14} cut was analyzed by standard GLC (carbowax column). The branched $C_{14}OH$ was 0.96% of normal $C_{14}OH$.

Run 2. The above method was repeated except the growth product was treated at 130-150° C. After work up and analysis as above, the branched $C_{14}OH$ was 1.8% of the normal $C_{14}OH$.

10 Having thus described our invention, we claim:

1. In the process wherein alcohols are prepared by oxidation of aluminum trialkyls to aluminum trialkoxides, the oxidation product is stripped by vaporization to remove by-products and thereafter hydrolyzed to alcohols, the improvement comprising stabilizing said aluminum trialkoxides against degradation during said stripping operation which comprises adding to said alkoxide from 2 to 7 weight percent of a stabilizing agent which is an aluminum trialkyl in which each alkyl contains 2 to 4 carbon atoms, an alkyl aluminum hydride in which each alkyl contains 2 to 4 carbon atoms or an alkali metal or aluminum hydride.

2. The improvement of claim 1 wherein the aluminum trialkoxide contains an average of at least 8 carbon atoms in the alkoxide groups.

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