

Inventors: Harold E. Marsh, Jr.
John J. Mulchison

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TRIFUNCTIONAL ALCOHOL

Organic compounds having three or more reactive sites are particularly useful in polymerization to cross-link various monomers. One of the most desirable reactive sites is the alcohol or hydroxyl grouping. Such alcohol end groups are particularly useful for cross-linking polyurethane resins. Thus, it is an object of this invention to provide a new trifunctional alcohol and novel method of preparing same.

The trifunctional alcohol of the invention is derived from trimer acid which contains about 54 carbon atoms and has three carboxylic groupings. To prepare the alcohol, the trimer acid is first converted to an ester form by reacting it with an alcohol. The ester groups of the triester are then subsequently converted to hydroxyl ones to provide the product of the invention. The conversion to hydroxyl groups is accomplished by either hydrogenating the triester or treating the ester with lithium aluminum hydride.

Prior to the herein invention, other trifunctional alcohols have existed. However, they were not satisfactory for cross-linking various monomers. Among the disadvantages of the prior alcohols was that some were not readily soluble in monomers. Others often had double bonds present which presented problems of controlling the cross-linking reaction. Further, some alcohols had the functional alcohol groups too closely spaced within the compound and hindered the possible cross-linking reaction. The trifunctional alcohol of this invention overcomes all the foregoing difficulties. Further, the method of preparation and particularly the utilization of lithium aluminum hydride provides high yields of the alcohol and unexpectedly increases the theoretical functionality of the alcohol over that of the trimer acid by apparently converting some aldehyde groups present in the trimer acid to hydroxyl ones.

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S P E C I F I C A T I O N

TO ALL WHOM IT MAY CONCERN:

BE IT KNOWN THAT, HAROLD E. MARSH, JR., residing at La Canada in the County of Los Angeles, State of California, and JOHN J. HUTCHISON, residing at Flushing in the County of Queens, State of New York, both citizens of the United States of America, have invented a new and useful

TRIFUNCTIONAL ALCOHOL

of which the following is a specification.

ABSTRACT OF THE DISCLOSURE

A new trifunctional alcohol made by first converting trimer acid to an ester form, and either treating the ester with a lithium aluminum hydride or hydrogenating it to form the end alcohol.

ORIGIN OF THE INVENTION

The invention described herein was made in the performance of work under a NASA contract and is subject to the provisions of Section 305 of the National Aeronautics and Space Act of 1958, Public Law 83-568 (72 Stat. 435; 42 USC 2457).

BACKGROUND OF THE INVENTION

1. Field of the Invention:

This invention is in the field of a new chemical compound and its method of manufacture. More particularly, the invention relates to a new trifunctional alcohol and two alternative methods of making the same.

2. Description of the Prior Art:

Organic compounds having three or more reactive sites are useful in polymerization for cross linking various monomers.

1 One of the most desirable reactive sites is the alcohol or
2 hydroxyl grouping. Alcohol end groups are particularly useful
3 for polyurethanes. Thus there is significant interest in
4 trifunctional alcohols as cross linking agents. Typical
5 trifunctional alcohols utilized prior to the herein invention
6 included trimethylolpropane, also known as TMP, and 1,2,6-hexane
7 triol. The disadvantage of TMP is that it is solid and hence
8 is not readily blendable to be intermixed with various
9 monomers without first being dissolved in a suitable solvent.
10 The triol, though a liquid, however, is not readily soluble
11 in various monomeric materials such as polyethers and the
12 like, in which it is desirable to achieve a cross linking.
13 Other trifunctional materials often have double bonds present
14 or unsaturated materials which present problems in controlling
15 the cross linking reaction or the subsequent environmental
16 stability.

17 A further disadvantage of previous trifunctional or
18 multifunctional alcohols relates to the closeness of the
19 alcohol groups in the structure. More effective cross linking
20 occurs when the functional groups are not too closely spaced
21 in the alcohol compound. If the alcohol reactive sites are
22 too closely spaced, hindrance can occur in that not all the
23 sites are available for the cross linking reaction, thus
24 preventing successful end results.

25 In forming alcohols, one often reduces an acid grouping.
26 However, in converting from an acid to an alcohol it has been
27 extremely difficult to obtain a quantitative chemical conversion
28 of the acid groups to the desired alcohol ones. If one is
29 particularly desirous of obtaining a trifunctional alcohol
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1 DESCRIPTION OF THE PREFERRED
2 EMBODIMENTS

3 Trimer acid is a name which is used to describe a high
4 molecular weight tribasic acid. It is a nearly saturated
5 material containing 54 carbon atoms. This acid is a stable
6 viscous liquid which is resistant to high temperatures. In
7 the past it has been combined with alcohols, polyols and
8 other reagents to make a variety of products such as plasti-
9 cizers, lube oils, and the like. Prior to the herein invention
10 there has not been reported an attempt to convert the trimer
11 acid to a corresponding trifunctional alcohol in a pure state.

12 One of the important uses for the trifunctional alcohol
13 of this invention is as a cross linking agent for polyurethane
14 resins. Polyurethanes are particularly useful as solid
15 propellant binders and in case liners for solid propellant
16 motors. To serve as a successful cross linking agent it is
17 apparent that the functionality of the alcohol should be about
18 3.0. A cross linked network can only be achieved through the
19 utilization of materials that have functionalities in excess
20 of 2. The closer the material approaches a functionality of
21 3.0, the tighter or more closely cross linked network can
22 be achieved since, as is apparent, there are more reactive
23 sites present.

24 The starting trimer acid is preferably one of a low
25 iodine value, since as indicated it is generally undesirable
26 to have unsaturated hydrocarbons in a cross linking reaction.
27 Thus, commercially obtained acid can first be hydrogenated
28 to lower the iodine value to a minimum. The following
29 esterification is accomplished by mixing the trimer acid with
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1 a large excess of either ethyl or methyl alcohol in a standard
2 glass esterification apparatus. The apparatus is equipped
3 with a condenser and condensate separation unit so that
4 the water formed could be removed by azeotropic distillation.
5 About 20% by volume of toluene is added to form the azeotrope.
6 A small quantity of sulphuric acid which can vary from 0.01
7 to 1.00 percent by volume is additionally added as a catalyst.
8 The mixture is then refluxed from one hour to 7 days. Water
9 is removed during the reaction by separation of the ternary
10 azeotrope distillate and recycling of the toluene layer at
11 periodic intervals. After completion of the reflux, the
12 mixture is then cooled and the acid catalyst extracted with
13 a sodium bicarbonate wash or similar technique. The resulting
14 trimer acid ester is a non-viscous oil with a very low
15 carboxyl content.

16 The trimer acid ester can be converted to the tri-
17 functional alcohol, as previously indicated, by hydrogenation
18 process. The ester is mixed with 0.1 to 10.0 weight percent
19 of a suitable catalyst such as copper chromium oxide. This
20 mixing is carried out in a pressure reactor. During the
21 mixing the temperature is raised to about 20° to 150°C, while
22 the pressure through a hydrogen inlet is raised to at least
23 4000 psi and preferably between 4500 and 5000 psi. Mixing
24 is continued throughout the entire reaction period. In about
25 from one hour to three days, the reaction is completed as
26 indicated by reduction of the take-up rate of hydrogen to the
27 pre-established leakage rate. The autoclave is then cooled and a
28 very viscous mass results. The resulting viscous mass is
29 initially filtered through a bed of diatomaceous earth to
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1 remove a portion of the copper and chromium compounds. It
2 is then further subjected to successive repeated extractions
3 of an ether solution, with ammonium hydroxide, hydrochloric
4 acid and saturated sodium bicarbonate solution in water. The
5 series of extractions is performed rapidly to minimize hydrolysis
6 of ester groups to carboxyl ones.

7 A more preferred synthesis of the trifunctional alcohol
8 of this invention comprises a reduction of the ester with
9 lithium aluminum hydride. In this process, the triester is
10 initially dissolved in a suitable solvent therefor. An
11 example of such a solvent is anhydrous diethylether. Other
12 solvents include other ethers. The solution of the triester
13 is then slowly added with stirring to a slurry of aluminum
14 hydride in a solvent therefor which can also be diethyl ether.
15 In order to assure the conversion to the alcohol, a large
16 excess of lithium aluminum hydride over that stoichiometrically
17 required is utilized. The reaction is kept at room temperature
18 and upon standing for a period of 24 hours, a thick precipitate
19 results. This precipitate is then hydrolized by dropwise
20 addition of water, followed by a dilute sulphuric acid. The
21 end trifunctional alcohol product is finally recovered from
22 the ether layer after washing with a suitable solution such as
23 sodium bicarbonate and water. The resulting product utilizing
24 this method has no trace of remaining carboxyl groups.

25 One of the most important advantages of the method of
26 making the trifunctional alcohol utilizing lithium aluminum
27 hydride lies in the high functionality of the resulting
28 alcohol. It has been found that the functionality of the
29 alcohol is significantly above the functionality of the starting
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1 trimer acid. This result might have occurred because the
2 trimer acid as obtained contained aldehyde groups in some
3 sites which would have been occupied by carboxyl groups.
4 Alternatively, during the hydrogenation purification process
5 applied to the trimer acid, aldehyde groups could have
6 possibly resulted.

7 It is believed that the invention will be better under-
8 stood from the following specific examples:

9 EXAMPLE I

10 A commercially available nearly saturated form of trimer
11 acid was obtained. This acid is prepared from the trimerization
12 of a C-18 fatty acid. It is denoted as Empol 1040 grade trimer
13 acid made by Emery Industries. The acid was then hydro-
14 genated until the iodine number of the resultant product was
15 less than 0.4. The hydrogenation was carried out at a
16 temperature between 110° and 140°C at a pressure of 1800 to
17 2000 psi in an autoclave. The solvent used was cyclohexane.
18 The catalyst for the hydrogenation comprised 5 weight percent
19 of paladium on charcoal. The resulting hydrogenated trimer
20 acid of the aforementioned low iodine number was then ready
21 for utilization in forming the desired end product of this
22 invention.

23 EXAMPLE II

24 In order to form an ester from the trimer acid, one mole
25 of the trimer acid as prepared in Example I was mixed with
26 10 moles of ethyl alcohol. This amount of ethyl alcohol
27 comprises a significant excess over that stoichiometrically
28 required to convert the trimer acid to the ester. The mixture
29 took place in a standard glass esterification apparatus which
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1 was equipped with a condenser and condensate separation unit.
2 This enabled the water form to be removed by azeotropic
3 distillation. Additionally added to the mixture of trimer
4 acid and ethyl alcohol was 20% by volume of toluene. Toluene
5 was added to form the azeotrope. Additionally, 0.1 - 1.0 percent
6 of sulphuric acid was added to the mixture to serve as a
7 catalyst. Upon addition of the sulphuric acid the mixture was
8 then refluxed for a continuous period of seven days. During
9 the refluxing water was removed by separation of the ternary
10 azeotrope distillate and recycling of the toluene layer at
11 periodic intervals. After the refluxing, the mixture was then
12 allowed to cool to room temperature and the acid catalyst was
13 extracted with a sodium bicarbonate wash. The resulting
14 product was a trimer acid ethyl ester which was a non-viscous
15 oil having a carboxyl content of less than that discernable
16 by IR. When the same procedure is repeated utilizing methyl
17 alcohol instead of ethyl alcohol, a trimer acid methyl ester
18 is likewise obtained. The yield is about 95 percent of
19 theoretical, the remaining five percent being washing losses.

20 EXAMPLE III

21 In this example the trimer acid triethyl ester formed
22 in Example II was converted to the triol product of this
23 invention by hydrogenation. To accomplish this, 120 grams of
24 trimer acid triethyl ester of Example II was mixed with 20 grams
25 of copper, chromium, oxide catalyst in a stirred autoclave
26 pressure reactor having a capacity of 200 mm. The temperature
27 of the autoclave was raised to 250°C, while the hydrogen inlet
28 pressure was raised to 5000 psi. After four hours of mixing
29 with the hydrogen pressure maintained between 4500 and 5000 psi,
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1 the autoclave was then cooled. A viscous mass remained in
2 the autoclave. The mass was then passed through a bed of
3 powdered Celite to filter the remaining copper and chromium
4 compounds. The viscous oil after filtration through the Celite,
5 however, still had a significant amount of metal compounds.
6 Approximate content was about 0.02 weight copper and less than
7 0.001 weight percent chromium. This amount of metal compounds
8 would seriously affect the use of the triol as a cross linking
9 agent for polyurethane and the like in solid propellant
10 applications. Thus, to further remove these materials, the
11 oil was dissolved in diethyl ether. The ether solution was
12 then subjected to successive repeated extractions, utilizing
13 7 molar ammonium hydroxide, 4 molar hydrochloric acid, and
14 saturated sodium bicarbonate solution in water. The series
15 of extractions were performed rapidly in order to minimize
16 the hydrolysis of the ester groups to carboxyl. The reaction
17 gave a yield of 95%. Analysis of the alcohol indicated a
18 slight impurity which appeared to be a carboxyl compound with
19 a peak at 1720 cm^{-1} in the infrared spectrum. The hydroxyl
20 functionality of the product was 2.14 as compared to 2.65
21 for the original carboxyl compound. The theoretical function-
22 ality is 3.0.

23 EXAMPLE IV

24 In this example lithium aluminum hydride was utilized
25 to achieve a conversion of the ester of Example II to the
26 desired triol. To a reaction vessel was first added one liter
27 of anhydrous ethyl ether and 300 grams of lithium aluminum
28 hydride. The lithium aluminum hydride was slowly mixed in
29 the ether to form a slurry. To this slurry was then added
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1 100 grams of trimer acid ethyl ester as formed in accord
2 with Example II, which had been previously dissolved in 500
3 milliliters of anhydrous diethyl ether. The ester was added
4 slowly to the aluminum hydride slurry while mixing was con-
5 tinued throughout the addition period with mechanical mixers
6 mounted above the reaction vessel. Evaporation of the ether
7 kept the reaction at room temperature. A resulting thick
8 precipitate which formed immediately was allowed to stand
9 overnight and was then hydrolyzed by very careful dropwise
10 addition of water followed by dilute sulphuric acid.

11 During the addition of the water and the dilute sulphuric
12 acid, the product was continually stirred. The ether layer
13 was then separated, washed with aqueous sodium bicarbonate
14 solution and then with water. The ether was then evaporated,
15 yielding a liquid product which was identified as a C-54
16 branched hydrocarbon chain alcohol by infrared spectroscopic
17 analysis. The hydroxyl content of this product was 3.7 meq/g.
18 This value corresponds exactly with the theoretical function-
19 ality for the trifunctional alcohol from trimer acid. The
20 carboxyl content, however, of the hydrogenated trimer acid
21 starting material resulting from Example I had a functionality
22 of only about 2.65. Thus, apparently new functional sites
23 were produced.

24 Analysis by high resolution NMR showed all the hydroxyl
25 groups in the triol product to be primary and therefore terminal.
26 The hydroxyl groups did not exist prior to the reduction of the
27 ester. It is also hypothesized that some of the carboxyl sites
28 were initially occupied by aldehydes in the trimer acid as
29 obtained. In the method utilizing lithium aluminum hydride,
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1 these aldehydes were converted to hydroxy groups whereas they
2 were left untouched in the hydrogenation process described in
3 Example III. Thus, it is seen that the method set forth in
4 there herein example utilizing lithium aluminum hydride is to
5 be generally preferred over the hydrogenation one, particularly
6 when the functionality of the starting trimer acid is not 3.0.
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