

METHOD OF PREPARING HYDROXYALKYL HINDERED PHENOLIC ANTIOXIDANTS

Background of the Invention

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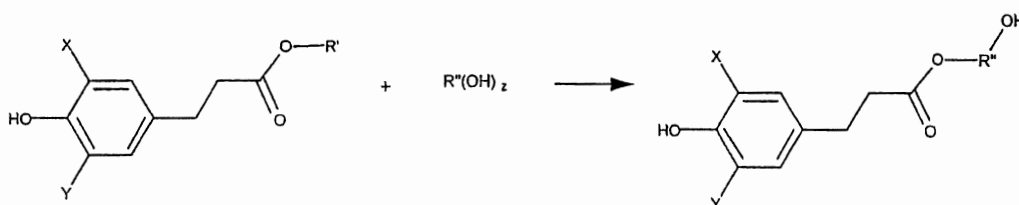
1. Field of the Invention

The present invention is directed to a method of preparing hindered phenolic antioxidants for lubrication oils or other organic media.

2. Description of Related Art

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Hydroxyalkyl hindered phenolic antioxidants are used as stabilizers for lubrication oils or other organic media. They are generally the reaction product between a starting ester and an alcohol with one or more hydroxyl groups to produce the following mono- ester product species:



15 wherein R' and R'' are hydrocarbon moieties.

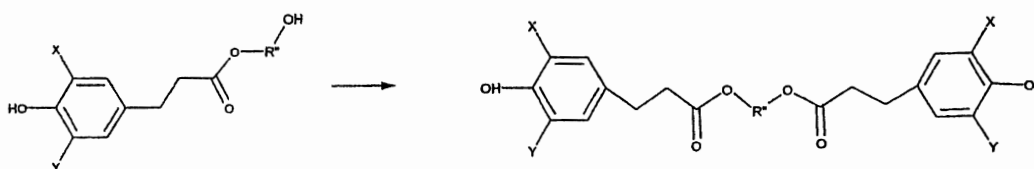
Typically, the phenolic antioxidants are prepared using transesterification catalysts such as para-toluene sulfonic acid which need to be washed out of the final product. However, this method requires numerous reaction steps and generates large amounts of waste. Other transesterification catalysts such as dibutyl tin diacetate or titanium isopropoxide are used as well but the problem remained in substantially removing traces of the catalyst once the reaction was terminated. If the amount of residual metal in the final product is too high, ultimate product stability is compromised, and costly, time consuming efforts must be taken to remove or reduce the amount of residual metal to a satisfactory level.

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U.S. Patent No. 5,892,097 to Ross et al. which issued on April 6, 1999, teaches a method of making esters of substituted

hydroxyhydrocinnamic acid useful as antioxidants by the transesterification of the corresponding methyl or ethyl ester with a higher aliphatic alcohol using small amounts of a tin catalyst, between 10 and 250 ppm based on an amount of the starting ester. The low catalyst level
 5 purportedly eliminates the need for post reaction separation of catalyst from the final ester product.

However, although the levels of tin are desirably low in Ross et al., during work up of a reaction between the phenolic ester and the alkanol or polyol, any live catalyst remaining in the reaction mixture would generate
 10 further reaction as illustrated below.



Reactions leading to the undesired bis- product species where the desired hydroxyl terminated mono- product species has further reacted are difficult to predict and control. Although the reaction may have proceeded
 15 to a majority of the mono- product species, during vacuum stripping of the solvents and/or alcohol, the remaining live catalyst promotes further reaction to the undesired bis- product species.

Bearing in mind the problems and deficiencies of the prior art, it is therefore an object of the present invention to provide a method of making
 20 hydroxyalkyl hindered phenolic antioxidants which uses low levels of metal catalyst and permits facile removal of most or all of the metal catalyst at the end of the reaction.

It is another object of the present invention to provide a method of making hydroxyalkyl hindered phenolic antioxidants wherein further
 25 reaction to the undesirable bis- product species is terminated or controlled.

It is yet another object of the present invention to provide a lubricating oil having a hydroxyalkyl hindered phenolic antioxidant with

exceedingly low residual tin or titanium levels such that product stability is not compromised.

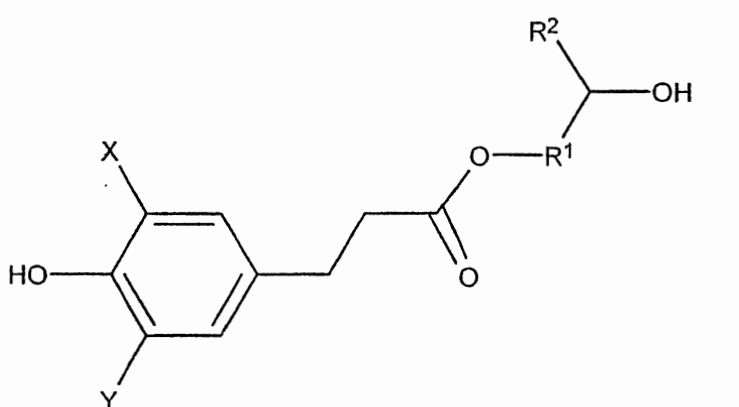
A further object of the invention is to provide hydroxyalkyl hindered phenolic antioxidants having exceedingly low residual tin or titanium levels such that post reaction processing is eliminated or reduced.

Still other objects and advantages of the invention will in part be obvious and will in part be apparent from the specification.

Summary of the Invention

The above and other objects and advantages, which will be apparent to one of skill in the art, are achieved in the present invention which is directed to, in a first aspect, a process of making a hindered phenolic antioxidant comprising:

providing an ester of formula I:



wherein X is H or a branched or linear alkyl hydrocarbon having 1 to 6 carbon atoms,

Y is H or a branched or linear alkyl hydrocarbon having 1 to 6 carbon atoms,

R¹ is a branched or linear alkyl having 1 to 12 carbon atoms, and

R² is H, or a branched or linear alkyl having 1 to 12 carbon atoms;

providing a diol having a primary hydroxyl group and a secondary or tertiary hydroxyl group;

providing a metal catalyst in an amount of about 20 to about 2000 ppm based on an amount of the ester;

heating the ester and the diol in the presence of the metal catalyst at a temperature of about 150 to 220°C such that the primary hydroxyl group of the diol reacts with the ester to form a desired mono- product species;

deactivating the metal catalyst; and

isolating the hindered phenolic antioxidant after deactivation such that conversion to a bis- product species is substantially reduced.

Preferably, the step of providing the diol comprises providing a diol selected from the group consisting of ethylene glycol, 1,2-propane diol, 1,3-propane diol, 1,2-butane diol, 1,3-butane diol, 1,4-butane diol, 2,3-butane diol, 1,2-pentane diol, 1,3-pentane diol, 1,4-pentane diol, 1,5-pentane diol, 2,3-pentane diol, 2,4-pentane diol, 1,2-hexane diol, 1,3-hexane diol, 1,4-hexane diol, 1,5-hexane diol, 1,6-hexane diol, 2,3-hexane diol, 2,4-hexane diol, and 2,5-hexane diol. It is also useful to provide an excess of the diol. The process of this aspect may further include the step of removing any residual diol after the step of deactivating the metal catalyst.

Preferably, the step of providing the metal catalyst comprises providing a metal catalyst selected from the group consisting of butyltin tris(2-ethylhexanoate), dibutyltin bis(2-ethylhexanoate), dibutyltin diacetate, dibutyltin oxide, trioctyltin oxide, butyltin trichloride, butyltin trimethylate, dibutyltin dichloride, diphenyltin dichloride, tributyltin chloride, stannous bis(2-ethylhexanoate), titanium (IV) titanates, including but not limited to ethyl titanate, n-propyl titanate, titanium isopropoxide, n-butyl titanate polymer, 2-ethylhexyl titanate, cresyl titanate, and titanium (IV) complexes, including, but not limited to, titanium acetyl acetonate, titanium lactic acid chelate, and titanium triethanolaminate isopropoxide.

In the step of isolating the hindered hydroxyalkyl phenolic antioxidant, a resultant hindered hydroxyalkyl phenolic antioxidant has a residual metal level of less than 80 ppm, and preferably less than 10 ppm, based on an amount of the hindered hydroxyalkyl phenolic antioxidant.

5 Preferably, the step of deactivating the metal catalyst comprises deactivating the metal catalyst with an oxidizing agent, which may also be followed by treating the hindered hydroxyalkyl phenolic antioxidant with acid treated clay to further reduce a residual metal level of the antioxidant. The oxidizing agent is preferably selected from the group
10 consisting of hydroperoxides, peroxides, manganese salts, oxygen, chlorine, perchlorates, and hypochlorites, wherein hydrogen peroxide is most preferred.

 The step of deactivating the metal catalyst may also comprise deactivating the metal catalyst with a reducing agent. Upon deactivation,
15 the residual metal level may be further reduced by treatment of the hindered hydroxyalkyl phenolic antioxidant with acid treated clay. The reducing agent is preferably selected from the group consisting of hydrazine or substituted hydrazines, sodium borohydride, lithium aluminum hydride, and borane complexes, wherein hydrazine or
20 substituted hydrazines are most preferred.

 As a one step process of deactivation and reduction of residual metal levels, one can use clay, acid treated clay, or acid treated bentonite clay. A residual metal content after the clay treatment is generally less than or equal to 6 ppm.

25 In another aspect, the present invention is directed to a method of making a hindered hydroxyalkyl phenolic antioxidant comprising the steps of:

 providing a hindered phenolic ester;
 providing, in excess, a diol having a primary hydroxyl group
30 and a secondary or tertiary hydroxyl group;

providing a tin or titanium catalyst in an amount of about 20 to about 500 ppm based on an amount of the ester;

heating the ester and the diol in the presence of the catalyst at a temperature of about 150 to 220°C such that the primary hydroxyl group of the diol reacts substantially with the ester;

deactivating the catalyst;

treating the product mixture with clay and filtering such that the resultant hindered hydroxyalkyl phenolic antioxidant has a residual tin or titanium level of less than 6 ppm; and

removing any residual diol after deactivation to isolate the product mixture.

Preferably, the step of providing a hindered phenolic ester comprises providing methyl-(3,5-di-t-butyl(4-hydroxyphenyl)) propionate.

Preferably, in the step of providing, in excess, a diol having a primary

hydroxyl group and a secondary or tertiary hydroxyl group, the diol is selected from the group consisting of ethylene glycol, 1,2-propane diol, 1,3-propane diol, 1,2-butane diol, 1,3-butane diol, 1,4-butane diol, 2,3-butane diol, 1,2-pentane diol, 1,3-pentane diol, 1,4-pentane diol, 1,5-pentane diol, 2,3-pentane diol, 2,4-pentane diol, 1,2-hexane diol, 1,3-hexane diol, 1,4-hexane diol, 1,5-hexane diol, 1,6-hexane diol, 2,3-hexane diol, 2,4-hexane diol, and 2,5-hexane diol. The tin catalyst is preferably selected from the

group consisting of butyltin tris(2-ethylhexanoate), dibutyltin bis(2-ethylhexanoate), dibutyltin diacetate, dibutyltin oxide, trioctyltin oxide, butyltin trichloride, butyltin trimethylate, dibutyltin dichloride,

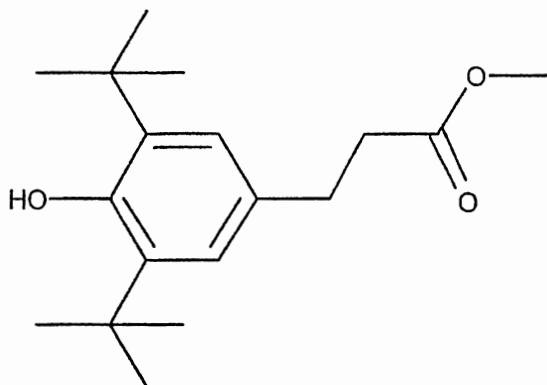
diphenyltin dichloride, tributyltin chloride, and stannous bis(2-ethylhexanoate). The titanium catalyst is preferably selected from the

group consisting of ethyl titanate, n-propyl titanate, titanium isopropoxide, n-butyl titanate polymer, 2-ethylhexyl titanate, cresyl titanate, titanium acetyl acetonate, titanium lactic acid chelate, and

titanium triethanolaminate isopropoxide.

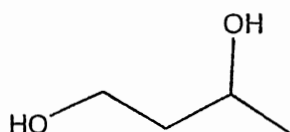
In yet another aspect, the present invention is directed to a method of making a hydroxyalkyl hindered phenolic antioxidant comprising:

providing an ester represented by



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5 providing a diol represented by



providing a tin or titanium catalyst in an amount of about 20 to about 500 ppm based on an amount of the ester;

10 heating the ester and the diol in the presence of the catalyst at a temperature of about 180 to 220°C for a sufficient time to effectuate transesterification;

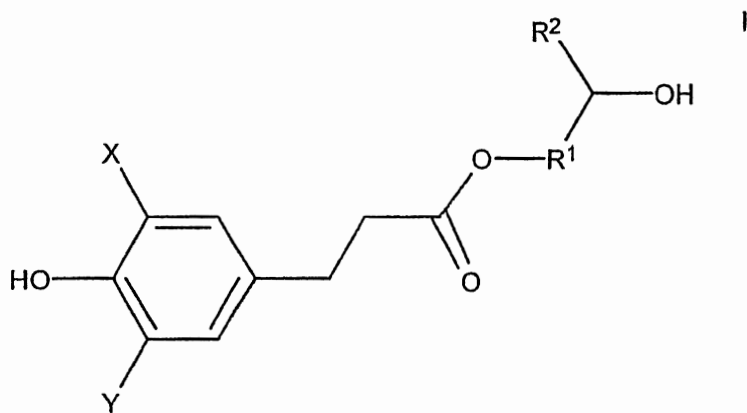
deactivating the catalyst with acid treated bentonite clay; and

isolating a reaction product having a residual tin or titanium content of less than or equal to 6 ppm.

15 Preferably, the step of providing a tin or titanium catalyst comprises providing a catalyst selected from the group consisting of butyltin tris(2-ethylhexanoate), dibutyltin bis(2-ethylhexanoate), dibutyltin diacetate, dibutyltin oxide, trioctyltin oxide, butyltin trichloride, butyltin trimethylate, dibutyltin dichloride, diphenyltin dichloride,
20 tributyltin chloride, stannous bis(2-ethylhexanoate), ethyl titanate, n-propyl titanate, titanium isopropoxide, n-butyl titanate polymer, 2-

ethylhexyl titanate, cresyl titanate, titanium acetyl acetate, titanium lactic acid chelate, and titanium triethanolaminate isopropoxide.

In still yet another aspect, the present invention is directed to a lubricating oil comprising a hindered phenolic antioxidant of formula I:



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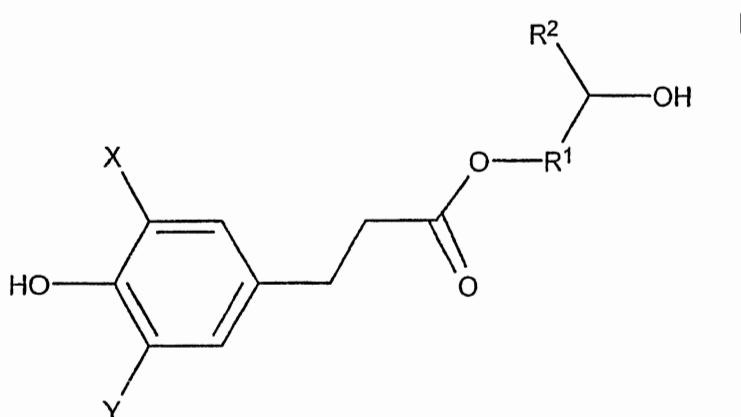
the hindered phenolic antioxidant having a residual metal content of less than 10 ppm based on the hindered phenolic antioxidant, wherein X is H or a branched or linear alkyl hydrocarbon having 1 to 6 carbon atoms; Y is H or a branched or linear alkyl hydrocarbon having 1 to 6 carbon atoms; R¹ is a branched or linear alkyl having 1 to 12 carbon atoms; and R² is H, or a branched or linear alkyl having 1 to 12 carbon atoms.

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Preferably, the hindered phenolic antioxidant has a residual metal content of equal to or less than 3 ppm.

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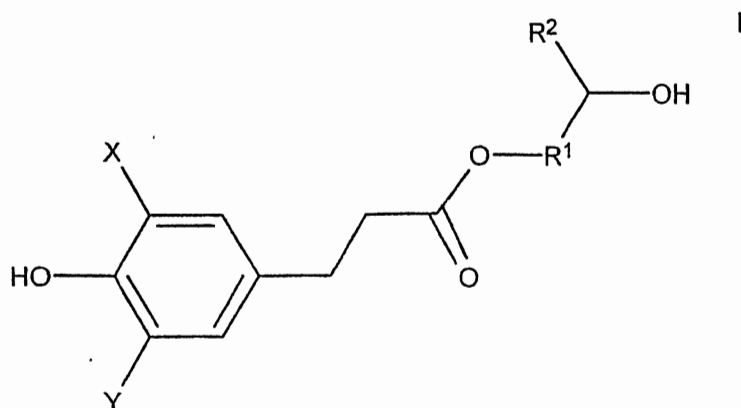
In a final aspect, the present invention is directed to a hydroxyalkyl hindered phenolic antioxidant of formula I:



having a residual metal content of less than 20 ppm based on an amount of the antioxidant, wherein X is H or a branched or linear alkyl hydrocarbon having 1 to 6 carbon atoms; Y is H or a branched or linear alkyl hydrocarbon having 1 to 6 carbon atoms; R¹ is a branched or linear alkyl having 1 to 12 carbon atoms; and R² is H, or a branched or linear alkyl having 1 to 12 carbon atoms.

Description of the Preferred Embodiment(s)

The present invention is directed to a method of making hindered phenolic antioxidants for lubrication oils or other organic media having the following general formula:



wherein X is H or a branched or linear alkyl hydrocarbon having 1 to 6 carbon atoms; Y is H or a branched or linear alkyl hydrocarbon having 1 to 6 carbon atoms; R¹ is a branched or linear alkyl having 1 to 12 carbon

atoms; and R^2 is H, or a branched or linear alkyl having 1 to 12 carbon atoms. X and Y may be the same or different. R^1 and R^2 may be the same or different. Preferably, X and Y are t-butyl. Preferably, R^1 has 1 to 3 carbon atoms. Preferably, R^2 is H, methyl, ethyl, propyl or butyl.

5 The compounds of formula I are made by reacting an ester with a diol in the presence of a metal transesterification catalyst. The diol preferably has a first primary hydroxyl group and a second hindered hydroxyl group. The hindered hydroxyl group may be a secondary or tertiary hydroxyl group. Preferred diols useful in the present invention
10 include ethylene glycol, 1,2-propane diol, 1,3-propane diol, 1,2-butane diol, 1,3-butane diol, 1,4-butane diol, 2,3-butane diol, 1,2-pentane diol, 1,3-pentane diol, 1,4-pentane diol, 1,5-pentane diol, 2,3-pentane diol, 2,4-pentane diol, 1,2-hexane diol, 1,3-hexane diol, 1,4-hexane diol, 1,5-hexane diol, 1,6-hexane diol, 2,3-hexane diol, 2,4-hexane diol, and 2,5-hexane diol.
15 More preferred are 1,2-propane diol, 1,2-butane diol, 1,3-butane diol, 1,2-pentane diol, 1,4-pentane diol, 1,2-hexane diol, and 1,5-hexane diol. The most preferred diols are 1,2-propane diol and 1,3-butane diol. The amount of diol is varied to control the amount of the desired product which is the hydroxyl-terminated mono-species. Low levels of the diol result in higher
20 levels of the undesirable bis- species wherein the ester has added twice to the diol. A useful molar ratio of ester to diol is about 1:0.9 to about 1:5, preferably about 1:1 to about 1:4.

Useful metal catalysts include butyltin tris(2-ethylhexanoate), dibutyltin bis(2-ethylhexanoate), dibutyltin diacetate, dibutyltin oxide,
25 trioctyltin oxide, butyltin trichloride, butyltin trimethylate, dibutyltin dichloride, diphenyltin dichloride, tributyltin chloride, stannous bis(2-ethylhexanoate), titanium (IV) titanates including, but not limited to, ethyl titanate, n-propyl titanate, titanium isopropoxide, n-butyl titanate polymer, 2-ethylhexyl titanate, cresyl titanate, and titanium (IV)
30 complexes, including, but not limited to, titanium acetyl acetonate,

titanium lactic acid chelate, and titanium triethanolaminate isopropoxide. Many of the titanium catalysts are commercially available from E.I. DuPont DeNemours Company, Wilmington, Delaware, under the TYZOR® tradename.

5 An effective amount of the catalyst is quite small, for tin, about 10 to about 200 ppm, preferably about 20 to about 100 ppm, and more preferably about 20 to 60 ppm, and for titanium about 50 to 3000 ppm, preferably about 100 to 1000 ppm and more preferably about 200 to 500 ppm, based on the amount of the ester. Using low levels of catalyst result
10 in correspondingly low levels of residual metal in the final product of about less than 3 to about 80 ppm, preferably less than about 30 ppm, and may be less than or equal to about 20 ppm based on an amount of the final product. The residual metal level may be further reduced as discussed below.

15 By running the reaction with excess diol at temperatures of about 150 to about 220°C, the diol reacts to form primarily the desired hydroxyl-terminated mono- product species rather than the undesirable bis- product species. Furthermore, by deactivating the catalyst prior to removing the residual excess diol, further reaction to the bis-species is advantageously
20 avoided. Subsequent removal of the residual diol by such means as vacuum stripping does not substantially alter the mono-/bis- product ratio once the catalyst is deactivated. Without deactivation of the catalyst prior to removal of the residual diol, however favorable the reaction is towards the desired mono- product species, further conversion to the undesirable
25 bis- product species during work up of the reaction is highly likely.

Deactivating the metal catalyst may be accomplished by using small amounts of oxidizing agents, reducing agents, or clay treatment. Suitable oxidizing agents of even moderate activity may be used to deactivate the metal catalyst including, but not limited to, peroxides, hydroperoxides
30 such as t-butyl hydroperoxide, manganese salts, oxygen, chlorine,

perchlorates, and hypochlorites including sodium hypochlorite. A most preferred oxidizing agent is hydrogen peroxide. An effective amount of the oxidizing agent to deactivate the metal catalyst may be expressed as the oxidizing agent to catalyst molar ratio of about 1:1 to about 10:1, preferably 2:1.

Suitable reducing agents include, but are not limited to, hydrazine, substituted hydrazines such as methyl hydrazine, sodium borohydride, metal hydrides including lithium aluminum hydride, and borane complexes including borane-t-butylamine complex. A most preferred reducing agent is hydrazine. An effective amount of the reducing agent to deactivate the metal catalyst may be expressed as the reducing agent to catalyst molar ratio of about 1:1 to about 10:1, preferably 2:1.

Clay, preferably acid treated clay, and most preferably acid treated bentonite clay, is an excellent means of deactivating the metal catalyst. It is understood that the term "bentonite" shall include all mineralogically related clays, such as smectites and montmorillonites, as set forth in the Kirk-Othmer Encyclopedia of Chemical Technology, 4th Edition, Vol. 6, pp. 381-405, the relevant portions of which are incorporated herein by reference. A preferred bentonite clay is commercially available as FILTROLTM from Engelhard Corporation of Jackson, Mississippi. Unexpectedly, when using the clay treatment, in particular acid treated clay, not only is the metal catalyst deactivated but, upon filtration, the residual metal level is also significantly lower so that additional steps which may be needed to further lower residual metal levels are unnecessary. The clay is likely to absorb the metal catalyst into its pores thereby physically preventing the catalyst from promoting further reaction. Advantageously, the use of acid treated clay, and more preferably acid treated bentonite clay, in deactivating and absorbing the metal catalyst also reduces the residual metal level of the product mixture to less than about 10 ppm based on an amount of the product mixture,

preferably to less than or equal to about 6 ppm, and most preferably to less than or equal to about 3 ppm. Thus, using clay, preferably acid treated clay, provides a two-fold benefit in deactivating the metal catalyst and substantially reducing residual metal levels.

5 Upon deactivation of the metal catalyst, during isolation of the ester product, preferably by vacuum distillation, the ratio of mono- product species to bis- product species remains substantially constant. There is no live catalyst to generate further reactions with the desired mono- product species.

10 By deactivating the metal catalyst prior to isolating the final product, there is little change in the ratio between the desired mono- product species and the undesirable bis- product species since further reaction with the mono- product species cannot occur. The method of the present invention also provides unexpectedly low levels of residual tin or
15 titanium in the final product mixture. The resultant product mixture can be used without further purification providing tremendous cost savings and efficiency in commercial processes, particularly when the acid treated bentonite clay is used to deactivate the metal catalyst. The resulting transesterification product may be used directly in subsequent synthesis
20 steps or as an ingredient in mineral oils and formulated mineral oils with much improved solubility.

Examples

25 The following Examples illustrate the preferred embodiments of the invention. They are not intended to limit the scope of the invention. Rather, they are presented merely to facilitate the practice of the invention by those of ordinary skill in the art.

Example 1 (Comparative)

Reaction of methyl (3,5-di-t-butyl-4-hydroxyphenyl) propionate and 1,2-propane diol.

This example illustrates the effect on the mono-/bis- product species ratio when the catalyst has not been deactivated prior to removing the excess diol.

In a 250mL 3-neck round bottom flask equipped with a Claisen adapter, an overhead stirrer and a short-path condenser, were combined 0.427 moles (125.0g) methyl (3, 5-di-t-butyl-4-hydroxyphenyl)propionate and 0.533 moles (40.6g) of 1,2-propane diol. On the Claisen adapter was a thermocouple and nitrogen inlet. A moderate nitrogen flow was maintained throughout the first part of the experiment. The reaction mixture was heated to 100°C and 0.68 mmols (0.24g) of dibutyl tin diacetate was added. The system was then heated to 170°C. After 16 hours the level of starting propionate was below 1% and the reaction was terminated. The nitrogen was discontinued and vacuum applied. The vacuum (28.5 in. Hg) was maintained at a temperature of 170°C for 20 minutes to strip away residual diol. Analysis of the product by gas chromatography before stripping showed 69.3 area% desired mono- species and 29.1 area% bis- species. After stripping the distribution changed to 35.4 area% mono- species and 63.9 area% bis- species.

Example 2 (Catalyst Deactivation with Hydrazine)

Reaction of methyl (3,5-di-t-butyl-4-hydroxyphenyl) propionate and 1,3-butane diol.

This example illustrates the use of a reducing agent, hydrazine monohydrate, to deactivate the tin catalyst.

In a 250mL 3-neck round bottom flask equipped with a Claisen adapter, an overhead stirrer and a knock-back condenser (70-75°C) followed by a distillation condenser and receiver, were combined 0.257

moles (75.0g) methyl (3,5-di-t-butyl-4-hydroxyphenyl) propionate and 0.772 moles (69.6g) of 1,3-butane diol. On the Claisen adapter was a thermocouple and nitrogen inlet. A moderate nitrogen flow was maintained throughout the first part of the experiment. The mixture was heated to 100°C and 0.39 mmols (0.14g) of dibutyl tin diacetate was added. The system was then heated to reflux conditions at 204°C. After 1.5 hours the level of starting propionate was below 1% and the reaction was terminated. The reaction was cooled to 50°C and 1.8 mmols (0.09g) hydrazine monohydrate was added. After 1 hour of agitation, the system was heated to 120°C. The nitrogen was turned off and vacuum applied. The vacuum (28.5 in. Hg) was maintained at a temperature of 120°C for 30 minutes to strip away residual diol. Analysis of the product by gas chromatography before stripping showed 78.5 area% mono-species and 21.5 area% bis-species. After stripping the product distribution was 80.2 area% mono-species and 19.8 area% bis-species. Clearly, there is no undesirable change in the ratio of the mono-/bis-species after removal of residual diol once the catalyst is deactivated.

Example 3 (Catalyst Deactivation with Hydrogen Peroxide)

Reaction of methyl (3,5-di-t-butyl-4-hydroxyphenyl) propionate and 1,3-butane diol.

This example illustrates the use of an oxidizing agent to deactivate the tin catalyst.

In a 2000mL 3-neck resin kettle reactor equipped with a Claisen adapter, an overhead stirrer and a knock-back condenser (70-75°C) followed by a distillation condenser and receiver, were combined 2.05 moles (600.0g) methyl (3,5-di-t-butyl-4-hydroxyphenyl) propionate and 6.16 moles (555.1g) of 1,3-butane diol. On the Claisen adapter was a thermocouple and nitrogen inlet. A moderate nitrogen flow was maintained throughout the first part of the experiment. The mixture was

heated to 100°C and 0.57 mmol (0.20g) of dibutyl tin diacetate was added. The system was then heated to reflux conditions at 204°C. After 4 hours the level of starting propionate was below 1% and the reaction was terminated. The reaction was cooled to 50°C and 1.1 mmol (0.13g of a 30wt.% solution) hydrogen peroxide was added. After 1 hour of agitation, the system was heated to 120°C. The nitrogen was turned off and vacuum applied. The vacuum (28.5 in. Hg) was maintained at a temperature of 120°C for 1 hour to strip away residual diol. Analysis of the product by gas chromatography before stripping showed 82.3 area% mono- species and 16.0 area% bis- species. After stripping, the product distribution was 82.7 area% mono- species and 16.4 area% bis- species. Clearly, there is no undesirable change in the ratio of the mono-/bis- species after removal of residual diol once the catalyst is deactivated.

Example 4 (Catalyst Deactivation with Hydrogen Peroxide & Residual Tin Removal With Acid Treated Bentonite Clay)

Reaction of methyl (3,5-di-*t*-butyl-4-hydroxyphenyl) propionate and 1,3-butane diol.

This example illustrates deactivation of the tin catalyst with an oxidizing agent and subsequent removal of residual tin with the acid treated bentonite clay to further lower the residual tin level.

In a 3000mL 3-neck round bottom flask equipped with a Claisen adapter, an overhead stirrer and a knock-back condenser (70-75°C) followed by a distillation condenser and receiver, were combined 4.28 moles (1250.0g) methyl (3,5-di-*t*-butyl-4-hydroxyphenyl) propionate and 12.83 moles (1157g) of 1,3-butane diol. On the Claisen adapter was a thermocouple and nitrogen inlet. A moderate nitrogen flow was maintained throughout the first part of the experiment. The mixture was heated to 100°C and 0.57 mmol (0.19g) of dibutyl tin diacetate was added. The system was then heated to reflux conditions at 200-204°C.

After 4.5 hours the level of starting propionate was below 1% and the reaction was terminated. The reaction was cooled to 50°C and 0.0013 moles (0.15g of a 30 wt.% solution) hydrogen peroxide was added. After 1 hour of agitation, the system was heated to 120°C. The nitrogen was
5 turned off and vacuum applied. The vacuum (28.5 in Hg) was maintained for 30 minutes at 120°C to strip off the excess diol. The nitrogen flow was reestablished and the reaction cooled to 110°C to which was added 10.0g of FILTROL™ 20x acid treated bentonite clay and 10.0g of diatomaceous earth filter aid. The reaction was agitated for 30 minutes and then
10 pressure filtered with a 1 micron filter disc at 100 psig nitrogen. Elemental analysis of the product before acid-clay treatment showed 19 ppm tin. Elemental analysis of the product after acid-clay treatment showed less than 3 ppm tin.

15 **Example 5 (Catalyst Deactivation & Residual Tin Removal with Acid Treated Bentonite Clay)**

Reaction of methyl (3,5-di-t-butyl-4-hydroxyphenyl) propionate and 1,3-butane diol.

This example illustrates the use of acid treated bentonite clay for
20 both deactivation of the tin catalyst and to lower residual tin levels.

In a 500mL 3-neck round bottom flask equipped with a Claisen adapter, an overhead stirrer and a knock-back condenser (70-75°C) followed by a distillation condenser and receiver, were combined 0.684 moles (200.0g) methyl (3,5-di-t-butyl-4-hydroxyphenyl) propionate and
25 2.053 moles (185.1g) of 1,3-butane diol. On the Claisen adapter was a thermocouple and nitrogen inlet. A moderate nitrogen flow was maintained throughout the first part of the experiment. The mixture was heated to 100°C and 0.15 mmol (0.054g) of dibutyl tin diacetate was added. The system was then heated to reflux conditions at 200-207°C.
30 After 5 hours the level of starting propionate was below 1% and the

reaction was terminated. The reaction was cooled to 120°C and 1.7g of FILTROL™ 20x (acid treated bentonite clay) and 3.3g of diatomaceous earth filter aid were added. The reaction mass was filtered after 30 minutes of agitation. The residual diol was removed by vacuum
5 distillation at 120°C for 1 hour. Analysis of the product by gas chromatography before stripping showed 87 area% mono- species and 13 area% bis- species. After stripping, the product distribution was 85 area% mono- species and 15 area% bis- species. Elemental analysis of the final product before acid clay treatment showed 60 ppm Sn. Analysis of the
10 final product after acid clay treatment showed less than 5 ppm residual tin.

Example 6 (Catalyst Deactivation and Residual Titanium Removal with Acid Treated Bentonite Clay)

15 Reaction of methyl (3,5-di-t-butyl-4-hydroxyphenyl) propionate and 1,3-butane diol with titanium (IV) (triethanolaminate) isopropoxide catalyst.

This example illustrates the use of acid treated bentonite clay for deactivation of the titanium catalyst and removal of residual titanium.

20 In a 250mL 3-neck round bottom flask equipped with a thermocouple adapter were combined 0.276 mol (80.45g) methyl (3,5-di-t-butyl-4-hydroxyphenyl) propionate and 1.14 mol (185.1g) of 1,3-butane diol. The flask was fitted with a thermocouple, a subsurface fritted glass nitrogen inlet, an overhead stirrer and a knock-back condenser (70-75°C)
25 followed by a distillation condenser and receiver. A moderate nitrogen flow was maintained throughout the first part of the experiment. The mixture was heated to 82°C and 0.66 mmol (0.192g) of TYZOR® TE titanium (IV) triethanolaminate isopropoxide (obtained from E. I. DuPont DeNemours Company) was added. The system was then heated at 190°C
30 for 3.8 hours. When the level of starting propionate was below 1%, the

reaction was terminated. The reaction was cooled to 120°C and 4.0g. FILTROL™ 20X (acid treated bentonite clay) was added. The reaction mass was stirred for 30 minutes and then filtered. The residual diol was removed by vacuum distillation at 132-140°C for 90 minutes. Analysis of the product by gas chromatography before clay treatment showed 93.0 area% mono-species and 6.7 area% bis-species. After stripping, the product distribution was 92.9 area % mono-species and 6.8 area % bis-species. Elemental analysis of the product before acid clay treatment showed 108 ppm titanium. Analysis of the filtered, clay treated product showed less than 3 ppm residual titanium.

Example 7 (Catalyst Deactivation & Residual Titanium Removal with Acid Treated Bentonite Clay)

Reaction of methyl (3,5-di-*t*-butyl-4-hydroxyphenyl) propionate and 1,3-butane diol with titanium (IV) isopropoxide catalyst.

This example illustrates the use of acid treated bentonite clay for deactivation of the titanium catalyst and removal of residual titanium.

In a 250mL 3-neck round bottom flask equipped with a thermocouple adapter were combined 0.276mol (80.52g) methyl (3,5-di-*t*-butyl-4-hydroxyphenyl) propionate and 0.875mol (78.72g) of 1,3-butane diol. The flask was fitted with a thermocouple, a subsurface fritted glass nitrogen inlet, an overhead stirrer and a knock-back condenser (70-75°C) followed by a distillation condenser and receiver. A moderate nitrogen flow was maintained throughout the first part of the experiment. The mixture was heated to 120°C and 0.72mmol (0.212g) of TYZOR® TPT titanium (IV) isopropoxide (obtained from E. I. DuPont DeNemours Company) was added. The system was then heated at 190°C for 4.0 hours. When the level of starting propionate was below 1%, the reaction was terminated. The reaction was cooled to 120°C and 4.0 g. FILTROL™ 20X (acid treated bentonite clay) was added. The reaction mass was stirred for

30 minutes and then filtered. The residual diol was removed by vacuum distillation at 130-140 °C for 40 minutes. Analysis of the product by gas chromatography before clay treatment showed 90.8 area % mono-species and 9.0 area % bis-species. After stripping, the product distribution was
5 90.4 area % mono-species and 9.4 area % bis- species. Elemental analysis of the product before acid clay treatment showed 190 ppm titanium. Analysis of the filtered, clay treated product showed less than 3 ppm residual titanium.

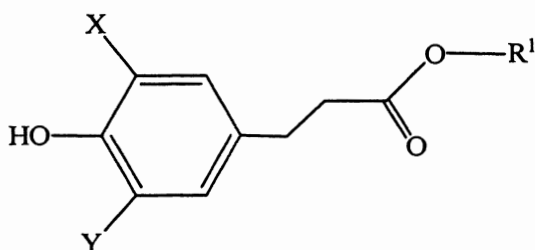
The present invention achieves the objects recited above. By
10 deactivating the metal catalyst prior to removing any remaining diol in the transesterification reaction, the favorable mono-/bis- product species ratio is maintained. Deactivating the metal catalyst with acid treated bentonite clay provides a final product mixture with exceedingly low residual metal levels.

15 While the present invention has been particularly described, in conjunction with a specific preferred embodiment, it is evident that many alternatives, modifications and variations will be apparent to those skilled in the art in light of the foregoing description. It is therefore contemplated that the appended claims will embrace any such alternatives,
20 modifications and variations as falling within the true scope and spirit of the present invention.

Claims

What is claimed is:

1. A process of making a hindered phenolic antioxidant comprising:
providing an ester of formula I:



wherein X is H or a branched or linear alkyl hydrocarbon having 1 to 6 carbon atoms, Y is H or a branched or linear alkyl hydrocarbon having 1 to 6 carbon atoms, and R¹ is a branched or linear alkyl having 1 to 12 carbon atoms;

providing a diol having a primary hydroxyl group and a secondary or tertiary hydroxyl group;

providing a metal catalyst in an amount of about 20 to about 2000 ppm based on an amount of the ester;

heating the ester and the diol in the presence of the metal catalyst at a temperature of about 150 to 220°C such that the primary hydroxyl group of the diol reacts with the ester to form a desired mono-product species;

deactivating the metal catalyst; and

isolating the hindered phenolic antioxidant after deactivation such that conversion to a bis- product species is substantially reduced.

2. The method of claim 1 wherein the step of providing the diol comprising providing a diol selected from the group consisting of ethylene glycol, 1,2-propane diol, 1,3-propane diol, 1,2-butane diol, 1,3-butane diol, 1,4-butane diol, 2,3-butane diol, 1,2-pentane diol, 1,3-pentane diol, 1,4-pentane diol, 1,5-pentane diol, 2,3-pentane diol, 2,4-pentane diol, 1,2-hexane diol, 1,3-hexane diol, 1,4-hexane diol, 1,5-hexane diol, 1,6-hexane diol, 2,3-hexane diol, 2,4-hexane diol, and 2,5-hexane diol.

3. The method of claim 1 wherein the step of providing the diol comprises providing an excess of the diol.

4. The method of claim 3 further including the step of removing any residual diol after the step of deactivating the metal catalyst.

5. The method of claim 1 wherein the step of providing the metal catalyst comprises providing a metal catalyst selected from the group consisting of butyltin tris(2-ethylhexanoate), dibutyltin bis(2-ethylhexanoate), dibutyltin diacetate, dibutyltin oxide, trioctyltin oxide, butyltin, trichloride, butyltin trimethylate, dibutyltin dichloride, diphenyltin dichloride, tributyltin chloride, stannous bis(2-ethylhexanoate), ethyl titanate, n-propyl titanate, titanium isopropoxide, n-butyl titanate polymer, 2-ethylhexyl titanate, cresyl titanate, titanium acetyl acetonate, titanium lactic acid chelate, and titanium triethanolaminate isopropoxide,

6. The method of claim 1 wherein in the step of isolating the hindered hydroxyalkyl phenolic antioxidant, a resultant hindered hydroxyalkyl phenolic antioxidant has a residual metal level of less than 80 ppm based on an amount of the hindered hydroxyalkyl phenolic antioxidant.

7. The method of claim 1 wherein in the step of isolating the hindered hydroxyalkyl phenolic antioxidant, a resultant hindered hydroxyalkyl phenolic antioxidant has a residual metal level of less than 10 ppm based on an amount of the hindered hydroxyalkyl phenolic antioxidant.

8. The method of claim 1 wherein the step of deactivating the metal catalyst comprises deactivating the metal catalyst with an oxidizing agent or a reducing agent.

9. The method of claim 8 further including the step of treating the hindered hydroxyalkyl phenolic antioxidant with clay, acid treated clay, or acid treated bentonite clay to further reduce a residual metal level of the antioxidant.

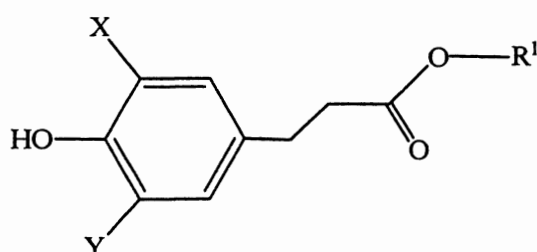
10. The method of claim 8 wherein the step of deactivating the metal catalyst with an oxidizing agent comprises deactivating the metal catalyst with an oxidizing agent selected from the group consisting of peroxides, hydroperoxides, manganese salts, oxygen, chlorine, perchlorates, and hypochlorites.

11. The method of claim 8 wherein the step of deactivating the metal catalyst with a reducing agent comprises deactivating the metal catalyst with a reducing agent selected from the group consisting of hydrazine or substituted hydrazines, sodium borohydride, metal hydrides, and borane complexes.

12. The method of claim 1 wherein the step of deactivating the metal catalyst comprises providing clay, acid treated clay, or acid treated bentonite clay.

13. A method of making a hindered hydroxyalkyl phenolic antioxidant comprising the steps of:

providing a hindered phenolic ester of formula I



wherein X is H or a branched or linear alkyl hydrocarbon having 1 to 6 carbon atoms, Y is H or a branched or linear alkyl hydrocarbon having 1 to 6 carbon atoms, and R¹ is a branched or linear alkyl having 1 to 12 carbon atoms;

providing, in excess, a diol selected from the group consisting of ethylene glycol, 1,2-propane diol, 1,3-propane diol, 1,2-butane diol, 1,3-butane diol, 1,4-butane diol, 2,3-butane diol, 1,2-pentane diol, 1,3-pentane diol, 1,4-pentane diol, 1,5-pentane diol, 2,3-pentane diol, 2,4-pentane diol, 1,2-hexane diol, 1,3-hexane diol, 1,4-hexane diol, 1,5-hexane diol, 1,6-hexane diol, 2,3-hexane diol, 2,4-hexane diol, and 2,5-hexane diol;

providing a tin or titanium catalyst in an amount of about 20 to about 500 ppm based on an amount of the ester;

heating the ester and the diol in the presence of the metal catalyst at a temperature of about 150 to 220°C such that the primary hydroxyl group of the diol reacts substantially with the ester;

deactivating the tin or titanium catalyst;

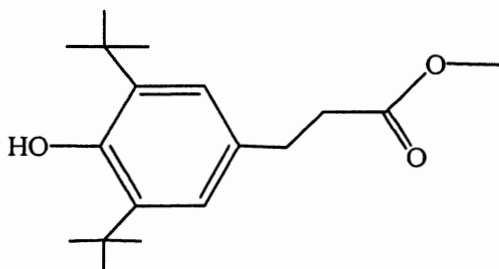
treating the product mixture with clay to provide the hindered hydroxylalkyl phenolic antioxidant having a residual tin or titanium level of less than 6 ppm; and removing any residual diol after deactivation to isolate the product mixture.

14. The method of claim 13 wherein the step of providing a hindered phenolic ester comprises providing methyl-(3, 5-di-t-butyl(4-hydroxyphenyl))propionate.

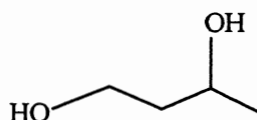
15. The method of claim 13 wherein the step of providing in excess, a diol comprises providing 1,2-propane diol, 1,2-butane diol, 1,3-butane diol, 1,2-pentane diol, 1,4-pentane diol, 1,2-hexane diol or 1,5-hexane diol.

16. The method of claim 13 wherein the step of providing a tin or titanium catalyst comprises providing a tin catalyst selected from the group consisting of butyltin tris (2-ethylhexanoate), dibutyltin bis(2-ethylhexanoate), dibutyltin diacetate, dibutyltin oxide, trioctyltin oxide, butyltin trichloride, butyltin trimethylate, dibutyltin dichloride, diphenyltin dichloride, tributyltin chloride, and stannous bis(2-ethylhexanoate), or a titanium catalyst selected from the group consisting of ethyl titanate, n-propyl titanate, titanium isopropoxide, n-butyl titanate polymer, 2-ethylhexyl titanate, cresyl titanate, titanium acetyl acetonate, titanium lactic acid chelate, and titanium triethanolaminate isopropoxide.

17. A method of making a hydroxyalkyl hindered phenolic antioxidant comprising:



providing a diol represented by



providing a tin or titanium catalyst in an amount of about 20 to about 500 ppm based on an amount of the ester;

heating the ester and the diol in the presence of the catalyst at a temperature of about 180 to 220°C for a sufficient time to effectuate transesterification;

deactivating the catalyst with acid treated bentonite clay; and

isolating a reaction product having a residual tin or titanium content of less than or equal to 6 ppm.

18. The method of claim 17 wherein the step of providing a tin a titanium catalyst comprises providing a tin catalyst selected from the group consisting of butyltin tris(2-ethylhexanoate), dibutyltin bis(2-ethylhexanoate), dibutyltin diacetate, dibutyltin oxide, trioctyltin oxide, butyltin trichloride, butyltin trimethylate, dibutyltin dichloride, diphenyltin dichloride, tributyltin chloride, and stannous bis(2-ethylhexanoate), or a titanium catalyst selected from the group consisting of ethyl titanate, n-propyl titanate, titanium isopropoxide, n-butyl titanate polymer, 2-ethylhexyl titanate, cresyl titanate, titanium acetyl acetonate, titanium lactic acid chelate, and titanium triethanolaminate isopropoxide.

19. A lubricating oil comprising a hindered phenolic antioxidant as defined in Claim 1, the hindered phenolic antioxidant having a residual metal content of less than 10 ppm, based on the hindered phenolic antioxidant.

20. A hydroxyalkyl hindered phenolic antioxidant as defined in Claim 1, having a residual metal content of less than 20 ppm based on an amount of the antioxidant.