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(54) Title: PROCESSES FOR PRODUCTION OF MACROMOLECULAR AMINE-PHENOLIC ANTIOXIDANT COMPOSITIONS CONTAINING LOW AMOUNTS OF NON-MACROMOLECULAR BYPRODUCTS

(57) Abstract: Processes are provided for producing macromolecular oxidation inhibitors that are almost free of low molecular weight components. Such processes comprise heating a combination comprising an aromatic amine, an acid catalyst, an alkylating agent, and a solvent to about 35°C to about 25O°C, thereby forming a reaction solution comprising one or more macromolecular amine-phenolic antioxidant solids and one or more non-macromolecular byproducts; combining at least the reaction solution and an antisolvent such that a precipitant comprising a substantial portion of the macromolecular amine-phenolic antioxidant solids precipitates out of the reaction solution, while a substantial portion of the non-macromolecular byproducts remain in the reaction solution; separating the precipitant from the reaction solution; and drying the precipitant to produce a MAPAC comprising less than about 1 wt.% non-macromolecular byproducts.

PROCESSES FOR PRODUCTION OF MACROMOLECULAR AMINE-PHENOLIC ANTIOXIDANT COMPOSITIONS CONTAINING LOW AMOUNTS OF NON-MACROMOLECULAR BYPRODUCTS

BACKGROUND

[0001] It is well known that a wide variety of organic materials are susceptible to oxidative degradation in the presence of air or oxygen, especially when at elevated temperatures. Such organic materials include, for example, gasolines, diesel fuels, burner fuels, gas turbine and jet fuels, automatic transmission fluids, base oils, gear oils, lubricants, engine lubricating oils, other industrial oils, polymer compositions, thermoplastic polymers, natural and synthetic rubber, and the like. Over the years, considerable efforts have been devoted to the discovery and development of compounds capable of minimizing the degradation of one or more of such materials. The majority of such compounds have molecular weights lower than 600. It is well established in the literature (Van Gestel, C.A.M., K. Otermann, and J.H. Canton; Regulatory, Toxicology, and Pharmacology, 1985, vol. 5, 422-431 and Zitko, V., Handbook of Environmental Chemistry, Vol. 2, Part A., Springer-Verlag, Berlin, pp 221-229) that molecules with molecular weight higher than 600 ("macromolecular" molecules) are generally too large to cross biological membranes and thus their potential for bioaccumulation is very low. As conditions of use of compounds for minimizing the degradation and exposure of such compounds to varying oxygen-containing environments change over the years, a desire for new effective oxidation inhibitors ("antioxidants") comprised of macromolecular compounds has developed. Also, the technology field benefits greatly if new and highly effective process technology is provided for producing known effective macromolecular oxidation inhibitors that are almost free of low molecular weight components.

[0002] Patent application publications WO2008/048987, WO2008/048989 and WO2008/048990 disclose and discuss a new class of macromolecular oxidation inhibitors and the preparation thereof. The macromolecular amine-phenolic antioxidant compositions ("MAPAC") described therein are hindered phenolic antioxidants that have an aminic backbone. The materials exhibit antioxidant behavior typical of both amines as well as phenolics. The new inhibitors perform well, but often contain appreciable levels of non-macromolecular byproducts, i.e., byproducts with molecular weights lower than 600, including for example, 4,4'-methylene-bis[2,6-di-t-butylphenol].

[0003] Thus, there is a need for processes of making and isolating the desired MAPACs while greatly reducing the levels of 4,4'-methylene-bis[2,6-di-t-butylphenol] and other non-macromolecular byproducts.

THE INVENTION

[0004] This invention meets the above-described needs by providing such processes. MAPACs comprising less than about 1 wt.% non-macromolecular byproducts, such as 4,4'-methylene-bis[2,6-di-t-butylphenol], can be obtained by processes of this invention.

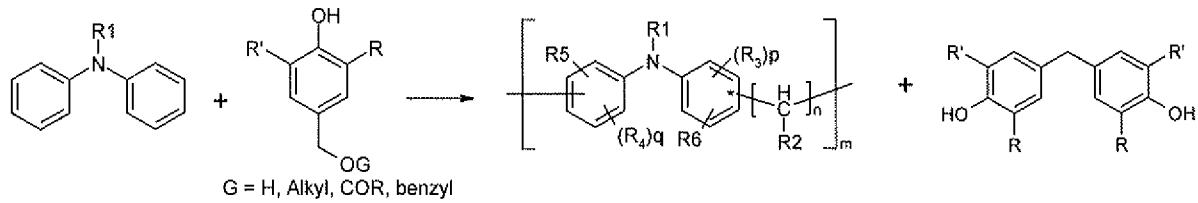
Also provided are such MAPACs, and base oils, polymer compositions, lubricant compositions, engine oils, and industrial oil compositions comprising such MAPACs.

[0005] Processes according to this invention can comprise: A) heating a combination comprising a secondary or tertiary aromatic amine, an acid catalyst, an alkylating agent, and a solvent to about 35°C to about 250°C, thereby forming a reaction solution comprising one or more macromolecular amine-phenolic antioxidant solids and one or more non-macromolecular byproducts; B) combining at least the reaction solution and an antisolvent such that a precipitant comprising a substantial portion of the macromolecular amine-phenolic antioxidant solids precipitates out of the reaction solution, while a substantial portion of the non-macromolecular byproducts remain in the reaction solution; C) separating the precipitant from the reaction solution; D)–optionally, filtering the precipitant to remove a substantial portion of the non-macromolecular byproducts; E) optionally, washing the precipitant to remove additional residual non-macromolecular byproducts; and F) drying the precipitant to produce a MAPAC comprising less than about 1 wt.% non-macromolecular byproducts, and optionally dissolving the MAPAC into a carrier oil or into the final desired product. As used herein, "macromolecular" indicates a molecule or compound having a molecular weight that is greater than 600, and "non-macromolecular" indicates a molecule or compound having a molecular weight that is less than 600. As used herein "a substantial portion" means at least about 30 wt% or higher, e.g., up to about 99 wt%.

[0006] Further, processes according to this invention can comprise: A) purifying a 4-substituted-2,6-di-t-butylphenol to reduce the amount of non-macromolecular impurities to less than about 5 wt%; B) heating a combination comprising the purified 4-substituted-2,6-di-t-butylphenol, diphenylamine, an acid catalyst, and an

alcohol to about 35°C to about 250°C, thereby forming a reaction solution comprising one or more macromolecular amine-phenolic antioxidant solids and one or more non-macromolecular byproducts; C) combining at least the reaction solution and an antisolvent such that a precipitant comprising a substantial portion of the macromolecular amine-phenolic antioxidant solids precipitates out of the reaction solution, while a substantial portion of the non-macromolecular byproducts remain in the reaction solution; D) separating the precipitant from the reaction solution; E) optionally, filtering the precipitant to remove a substantial portion of the non-macromolecular byproducts; F) optionally, washing the precipitant to remove additional residual non-macromolecular byproducts; and G) drying the precipitant to produce a MAPAC comprising less than about 1 wt.% non-macromolecular byproducts, and optionally dissolving the MAPAC into a carrier oil or into the final desired product.

[0007] The inventors hereof believe, while not wishing to be bound by theory, that the production of MAPACs may be described by the following scheme:



MAPACs Formation: Aromatic Amines

[0008] Any suitable aromatic amine may be used in processes of this invention. Suitable secondary aromatic amines include, without limitation, diphenylamine, phenylnaphthylamine, dinaphthylamine, phenyltolylamine, di-tolyl amine, tolylnaphthylamine, hydrocarbyl substituted diphenylamine, hydrocarbyl substituted phenylnaphthylamine, and hydrocarbyl substituted dinaphthylamine. Suitable tertiary amines include N-methyl diphenylamine, N-ethyl diphenylamine, N-propyl diphenylamine, N-butyl diphenylamine, triphenylamine, N-methyl phenylnaphthylamine, N-ethyl phenylnaphthylamine, N-propyl phenylnaphthylamine, N-butyl phenylnaphthylamine. Any of these amines having aromatic rings substituted with a hydrocarbyl substituent is also suitable.

MAPACs Formation: Acid Catalyst

[0009] Acid catalysts suitable for use in this invention may be organic or inorganic acids and may have pK_as less than -1.74. Acid catalysts such as sulphuric acid and methanesulfonic acid have been successfully used, and it is believed that other such acid catalysts will be equally effective. The choice and amount of acid catalyst used is driven by a desire for efficient and rapid conversion of the starting materials to the MAPACs molecules while at the same minimizing the formation of byproducts including 4,4'-methylene-bis[2,6-di-t-butylphenol]. The amount of acid catalyst charged can be kept between about 0.01 and about 1.5 moles of acid per mole of aromatic amine charged to minimize formation of byproducts while still resulting in an acceptable reaction rate. At lower loadings, the reaction is likely to be slow while at higher loadings, side reactions, including the formation of 4,4'-methylene-bis[2,6-di-t-butylphenol], may be significant.

MAPACs Formation: Alkylating Agents

[0010] Alkylating agents suitable for use in processes of this invention include, without limitation, 4-methoxymethyl-2,6-di-t-butylphenol, 4-hydroxymethyl-2,6-di-t-butylphenol, 4-acetoxymethyl-2,6-di-t-butylphenol, and other derivatives of the 4-hydroxymethyl-2,6-di-t-butylphenols, like 4-ethoxymethyl, 4-propoxymethyl, etc. or esters of propionic acid, butyric acid, etc. could also be used.

MAPACs Formation: Purification of Alkylating Agent

[0011] When a 4-substituted-2,6-di-t-butylphenol, such as 4-methoxymethyl-2,6-di-t-butylphenol, is used as the alkylating agent, it can be purified through a technique such as crystallization, distillation, e.g., under reduced pressure, flashing, or a simple wash with an appropriate solvent. Alternatively, it can be slurried in a hydrocarbon solvent like heptane followed by filtration and drying. The purpose of the purification is to reduce the carry through of impurities in the precursor and to minimize the production of additional low molecular weight (non-macromolecular) impurities during the MAPACs reaction. The non-macromolecular byproducts/impurities include, for example, 4,4'-methylene-bis[2,6-di-t-butylphenol]. It is desirable to use a

4-substituted-2,6-di-t-butylphenol with a purity of about 95 wt% or higher, e.g., up to about 99.9wt%.

[0012] 4-Substituted-2,6-di-t-butylphenols can be prepared from 2,6-di-t-butylphenol and formaldehyde in an appropriate solvent with base or acid catalysis. For example, if the reaction is carried out in methanol the major product is 4-methoxymethyl-2,6-di-t-butylphenol. By varying the solvent it is possible to prepare 4-hydroxymethyl-2,6-di-t-butylphenol, 4-acetoxymethyl-2,6-di-t-butylphenol, 4-ethoxymethyl-2,6-di-t-butylphenol, etc. A major competing reaction is the formation of 4,4'-methylene-bis[2,6-di-t-butylphenol]. Depending on reaction conditions, significant quantities, in the range of 1-50%, of this and other non-macromolecular byproducts may accompany the desired product. 4,4'-Methylene-bis[2,6-di-t-butylphenol] and some of the other byproducts will act as an inert in the MAPAC reaction and thus will carry through to the final product. As a result it is advantageous to remove the 4,4'-methylene-bis[2,6-di-t-butylphenol] and some of the other non-macromolecular components from the starting material. Processes that may be contemplated include, but are not limited to, crystallization, zone refining, flashing, and distillation.

[0013] In the case of 4-methoxymethyl-2,6-di-t-butylphenol, distillation under reduced pressure is desirable; e.g., unpurified 4-methoxymethyl-2,6-di-t-butylphenol with a purity of 70-90% may be batch distilled with minimal staging and reflux at up to 150°C and 2 Torr resulting in 4-methoxymethyl-2,6-di-t-butylphenol containing less than 0.1 wt.% 4,4'-methylene-bis[2,6-di-t-butylphenol] and purity of 97-99%.

MAPACs Formation: Temperature

[0014] The reaction temperatures should also be chosen to allow decent reaction rates while minimizing impurity formation. For the diphenylamine / 4-methoxymethyl-2,6-di-t-butylphenol system, one or more temperatures between about 35°C and 250°C can be used. At low temperatures, the reaction rate will be slow while at high temperatures it is likely that more impurities will be formed. Included among those impurities may be dealkylation products of the starting materials and products. These impurities are likely to have lower performance than non-dealkylated species. In all cases, the temperature(s) chosen should be such that the pressure of the system does not exceed the maximum allowable working pressure (MAWP) of the vessel containing the reaction mass.

MAPACs Formation: Addition of Alkylating Agent to Aromatic Amine

[0015] For exothermic reactions such as the formation of MAPACs, it is often times advisable at commercial scale to meter one reactant into the others so that the heat removal capabilities of the reactor can be matched with the heat generated from the reaction. For the present system, one possible but non-exclusive way of doing so is to feed the alkylating agent like 4-methoxymethyl-2,6-di-t-butylphenol into the amine. Another benefit of metering the alkylating agent like 4-methoxymethyl-2,6-di-t-butylphenol into the amine may be reduced formation of 4,4'-methylene-bis[2,6-di-t-butylphenol] or other non-macromolecular by products. In the presence of acid, 4-methoxymethyl-2,6-di-t-butylphenol reacts with itself to generate 4,4'-methylene-bis[2,6-di-t-butylphenol]. The rate of this reaction, while not specifically determined, is likely to be second order in regards to the concentration of 4-methoxymethyl-2,6-di-t-butylphenol and other non-macromolecular products. By metering the 4-methoxymethyl-2,6-di-t-butylphenol, the concentration of 4-methoxymethyl-2,6-di-t-butylphenol at any given time in the reactor will be low thus resulting in less 4,4'-methylene-bis[2,6-di-t-butylphenol] being produced.

Solvents and Antisolvents for MAPACs Formation and MAPACs Workup

[0016] Many solvents have been found to be acceptable for producing MAPACs including aromatic compounds such as toluene, alcohols such as methanol, and carboxylic acids such as acetic acid. Alcohols and potentially carboxylic acids lend themselves to post-reaction purification of MAPACs. It is possible to selectively precipitate MAPACs species from solutions of alcohols, such as methanol, by the addition of an antisolvent such as water. Byproducts such as 4,4'-methylene-bis[2,6-di-t-butylphenol] remain in solution and can be removed from the solid MAPACs via filtration. Further, when water is the antisolvent, the inventors have discovered that, unexpectedly, it is possible to preferentially enhance the solubility of the 4,4'-methylene-bis[2,6-di-t-butylphenol] in the mother liquor relative to other phenolic components through the addition of a strong base such as sodium hydroxide, potassium hydroxide, or the like. Not wishing to be bound by theory, the authors believe that the base deprotonates a portion of the 4,4'-methylene-bis[2,6-di-t-butylphenol] present and this deprotonated 4,4'-methylene-bis[2,6-di-t-butylphenol] is more soluble in the liquid phase than is the neutral 4,4'-methylene-bis[2,6-di-t-butylphenol]. A strong base can be a base having a pK_a greater than about 13.

[0017] If selective precipitation of MAPACs from alcohol/water mixtures is contemplated, methanol is desirable over higher alcohols due to ease of recycle. Other higher alcohols such as ethanol, propanols, butanols, etc. are also useful. At commercial scale it is important to recycle solvents to improve project economics as well as to be environmentally friendly. Unlike the other alcohols mentioned, methanol does not form an azeotrope with water which in turn makes methanol easier to recover in a pure form via distillation. Without taking additional steps, the other alcohols will contain some amount of water when recycled via distillation. This water may lead to increased levels of byproducts and also adversely affect the reaction rate in the MAPACs reaction.

MAPACs Precipitation

[0018] It is desirable to precipitate the MAPACs from solution by cofeeding the reaction solution and water, either with or without base, since the MAPACs tend to precipitate as particulates which are easily filtered or otherwise removed from solution.

[0019] The ratio of alcohol to antisolvent chosen when selectively precipitating MAPACs is dependent upon the specific alcohol and antisolvent chosen. With methanol as the solvent and water as the antisolvent, mass ratios between about 99:1 methanol:water and about 20:80 methanol:water can be used; ratios between about 85:15 and 50:50 being preferred. At higher ratios of methanol to water, the precipitated MAPACs are tar-like in nature rather than discrete particulates. This makes it more difficult to process the MAPACs downstream as they are not easily filtered or otherwise removed from solution. If the ratio of methanol to water is low, higher levels of byproducts, including 4,4'-methylene-bis[2,6-di-t-butylphenol], will be contained in the precipitated MAPACs.

[0020] Several permutations are possible in selectively precipitating the MAPACs from the solvent. The MAPACs solution may be fed into the antisolvent, the antisolvent may be fed into the MAPACs solution, or the MAPACs solution and antisolvent may be cofed to one another. For the methanol / water system, the latter technique keeps the ratio of solvent to antisolvent constant throughout. If the water is fed into the MAPACs solution, the initial concentration of methanol to water is high which may lead to tars. If the MAPACs solution is fed into the water, the initial

concentration of water is high which may encapsulate impurities within the precipitated MAPACs.

[0021] If a base is used during the precipitation to enhance the solubility of 4,4'-methylene-bis[2,6-di-t-butylphenol] in the mother liquor, the base chosen should be of sufficient strength that an appreciable amount of the 4,4'-methylene-bis[2,6-di-t-butylphenol] will be deprotonated. For the methanol/water system, sodium hydroxide has found utility in enhancing the solubility of the 4,4'-methylene-bis[2,6-di-t-butylphenol]. Strong bases such as potassium hydroxide and calcium hydroxide are expected to behave similarly.

[0022] If a base is used, the amount charged should be sufficient to at least neutralize all of the acid catalyst used in the formation of the MAPACs; that is the equivalents of base should be greater than the equivalents of acid charged. For the specific example of sodium hydroxide as base and sulphuric acid as catalyst, the amount of sodium hydroxide charged should be at least twice that of the sulphuric acid on a molar basis since sulphuric acid is diprotic. The upper limit on the amount of base to use will be dependent upon the specific base and precipitation medium with the cost of the base, the solubility of the base in the medium, and the relative amount of byproducts being removed all being important factors.

Washing of Precipitated MAPACs

[0023] While the washing step is optional, it is desirable if the highest purity MAPACs are to be isolated.

[0024] To minimize the complexity of solvent recycle, it is desirable to use as a wash solvent the same mixture of chemicals that were used in the precipitation step. As an example, if methanol is the solvent for the MAPACs reaction and water is used to precipitate the MAPACs from solution, the precipitated MAPACs can be washed with a mixture of methanol and water. The ratio of methanol to water used in the wash step is governed by the same issues involved with the precipitation of the MAPACs.

[0025] Filtering and washing can be used to isolate particularly pure MAPAC solids by removing non-macromolecular byproducts that precipitate out of the reaction solution along with the MAPAC solids.

Further Processing of MAPACs

[0026] Additional processing of the wet MAPACs is dependent upon the desired form that the end user will receive. Should the end user desire having the MAPACs in a dry, solid form, the wet MAPACs may be dried or the solvent contained within them may be flashed/distilled away. If the end user desires to have the MAPACs in a carrier oil, the MAPACs may be dried in the above manner and then put into the oil or the wet MAPACs may be first put into the oil and then solvent flashed/distilled away. Other permutations/combinations may be contemplated.

[0027] If the MAPAC solids are dissolved in a carrier oil or into the final product, they may optionally be dried either before or after they are dissolved. The drying provides MAPAC solids that are in a more easily handled form. Drying may be accomplished by any number of means including heating at atmospheric pressure, heating under reduced pressure, etc.

Macromolecular Amine-phenolic Antioxidant Solids of the Invention

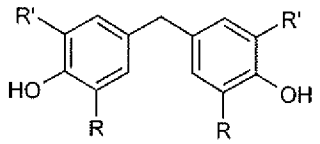
[0028] The macromolecular amine-phenolic antioxidant solids of the present invention typically comprise one or more alkylated aromatic amines, and one or more alkylated aromatic amines having one or more methylene bridge(s). The alkylated aromatic amines typically comprise one or more i) aromatic amines substituted with one 3,5-di-hydrocarbyl-4-hydroxylbenzyl groups, sometimes referred to herein as mono-alkylated aromatic amines; ii) aromatic amines substituted with two 3,5-di-hydrocarbyl-4-hydroxylbenzyl groups, sometimes referred to herein as di-alkylated aromatic amines; iii) aromatic amines substituted with three 3,5-di-hydrocarbyl-4-hydroxylbenzyl groups, sometimes referred to herein as tri-alkylated aromatic amines; iv) aromatic amines substituted with four 3,5-di-hydrocarbyl-4-hydroxylbenzyl groups, sometimes referred to herein as tetra-alkylated aromatic amines; v) aromatic amines substituted with five 3,5-di-hydrocarbyl-4-hydroxylbenzyl groups, sometimes referred to herein as penta-alkylated aromatic amines; vi) aromatic amines substituted with six 3,5-di-hydrocarbyl-4-hydroxylbenzyl groups, sometimes referred to herein as hexa-alkylated aromatic amines; and vii) one or more methylene-bridged aromatic amines substituted with one or more 3,5-di-hydrocarbyl-4-hydroxylbenzyl groups. The macromolecular amine-phenolic antioxidant solids of the present invention can contain less than about 5wt.% of aromatic amines substituted with one 3,5-di-hydrocarbyl-4-hydroxylbenzyl groups,

based on the total weight of the macromolecular amine-phenolic antioxidant solids. The macromolecular amine-phenolic antioxidant solids of the present invention can contain 10wt.% or less of aromatic amines substituted with two 3,5-di-hydrocarbyl-4-hydroxylbenzyl groups. The macromolecular amine-phenolic antioxidant solids of the present invention can contain 5wt.% or less of aromatic amines substituted with one 3,5-di-hydrocarbyl-4-hydroxylbenzyl groups and aromatic amines substituted with two 3,5-di-hydrocarbyl-4-hydroxylbenzyl groups, on the same basis. The macromolecular amine-phenolic antioxidant solids of the present invention can comprise greater than 40wt.%, or greater than about 45wt.%, or greater than about 50wt.%, of aromatic amines substituted with four 3,5-di-hydrocarbyl-4-hydroxylbenzyl groups, aromatic amines substituted with five 3,5-di-hydrocarbyl-4-hydroxylbenzyl groups, or aromatic amines substituted with six 3,5-di-hydrocarbyl-4-hydroxylbenzyl groups, all based on the total weight of macromolecular amine-phenolic antioxidant solids. The macromolecular amine-phenolic antioxidant solids of the present invention can contain in the range of from about 1 to about 20wt.%, or in the range of from about 1 to about 15wt.%, or in the range of about 1 to 10 wt% of one or more methylene-bridged aromatic amines substituted with one or more 3,5-di-hydrocarbyl-4-hydroxylbenzyl groups, all based on the total weight of the macromolecular amine-phenolic antioxidant solids.

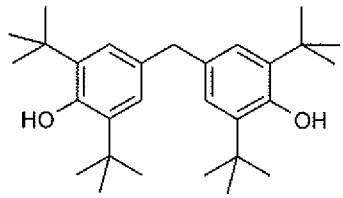
[0029] The macromolecular amine-phenolic antioxidant solids of the present invention can be described as comprising i) less than about 5wt.%; or less than about 1wt.%, or less than about 0.5wt.%, aromatic amines substituted with one 3,5-di-hydrocarbyl-4-hydroxylbenzyl groups, all based on the total weight of the macromolecular amine-phenolic antioxidant solids; ii) less than about 10wt.%; or less than about 5wt.%, or less than about 1wt.%, aromatic amines substituted with two 3,5-di-hydrocarbyl-4-hydroxylbenzyl groups, all based on the total weight of the macromolecular amine-phenolic antioxidant solids; iii) in the range of from about 1wt.% to about 35 wt.%, or in the range of from about 5wt.% to about 25 wt.%, or in the range of from about 5wt% to about 20wt.% aromatic amines substituted with three 3,5-di-hydrocarbyl-4-hydroxylbenzyl groups, on the same basis; iv) in the range of from about 10wt% to about 65 wt.%, or in the range of from about 15wt% to about 60wt.%, or in the range of from about 20wt% to about 55wt.% aromatic amines substituted with four 3,5-di-hydrocarbyl-4-hydroxylbenzyl groups, on the same basis; v) in the range of from about 5wt% to about 60wt.%, or in the range of from about

8wt% to about 50wt.%, or in the range of from about 10wt% to about 40wt.% aromatic amines substituted with five 3,5-di-hydrocarbyl-4-hydroxylbenzyl groups, on the same basis; vi) in the range of from about 1wt% to about 50 wt.%, or in the range of from about 5wt% to about 35wt.%, or in the range of from about 5wt% to about 20wt.% aromatic amines substituted with six 3,5-di-hydrocarbyl-4-hydroxylbenzyl groups, on the same basis; and vii) in the range of from about 1 to about 20 wt.%, or in the range of from about 1 to about 15wt.%, or in the range of from about 1wt% to about 10wt.% of one or more methylene-bridged aromatic amines substituted with one or more 3,5-di-hydrocarbyl-4-hydroxylbenzyl groups.

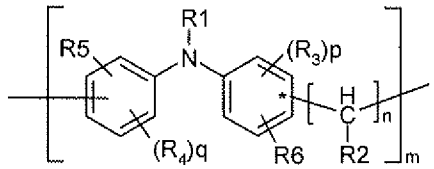
[0030] The macromolecular amine-phenolic antioxidant solids of the present invention can also contain in the range of from about 0.1 to about 1 wt.% of one or more phenolics represented by the following general structure:



wherein each R and R' are independently H or a hydrocarbyl. R and R' can be H or a straight or branched chain alkyl group. For example, R and R' can be tert-butyl and the compound is 4,4'-methylene-bis[2,6-di-t-butylphenol]:



[0031] The macromolecular amine-phenolic antioxidant solids of the present invention can comprise one or more compounds that can be represented by the following general structure:

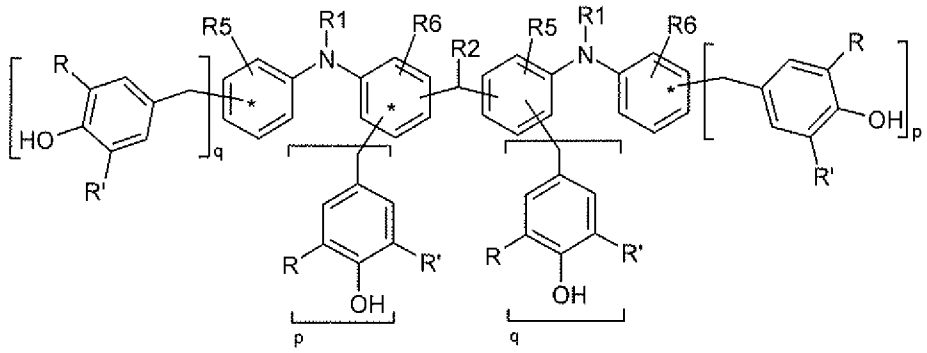


Structure I

wherein R_1 is H or hydrocarbyl, R_2 is H or hydrocarbyl, R_3 & R_4 are 3,5-dihydrocarbyl-4-hydroxybenzyl, R_5 and R_6 are H or hydrocarbyl, n is a whole number in the range

of from about 0 to about 1, p and q are whole numbers and p+q is in the range of from about 1 to about 10, and m is 1 when n=0 and m is a whole number in the range of from about 2 to about 10 when n=1. Macromolecular amine-phenolic antioxidant solids of the present invention can contain more than one molecule represented by the above-described general structure. Each of the one or more compounds can have the same or different constituents for R_1, R_2, R_3, R_4, R_5, and R_6 and each of the one or more compounds can have the same or different values for p, q, m, and n.

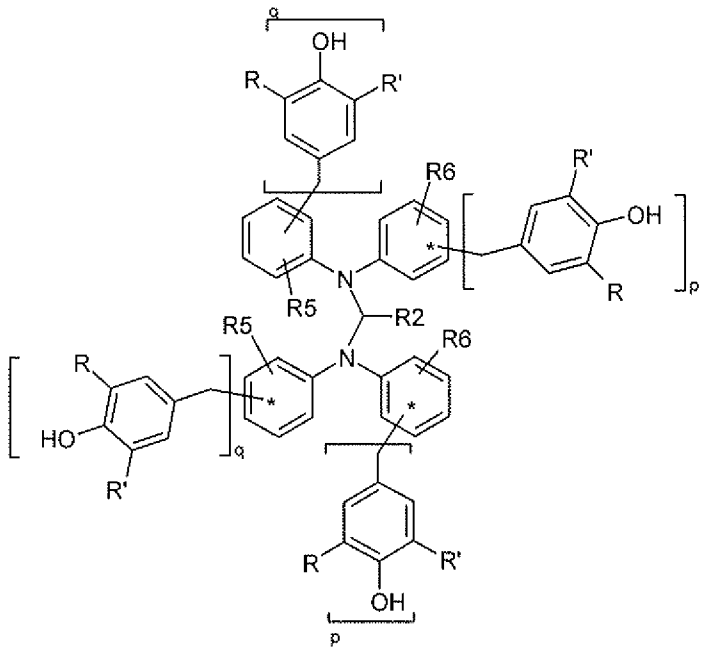
[0032] The macromolecular antioxidant compositions of the present invention can contain one or more, or two or more, compounds represented by the following general structure:



Structure II

wherein R_1, R_2, R_5, and R_6 of Structure II are independently H or hydrocarbyl, R & R' are independently hydrogen or a branched or straight chain alkyl containing in the range of from about 1 to about 8 carbons, or in the range of from about 1 to about 4 carbon atoms, and p and q are independently whole numbers in the range of from about 1 to about 10, wherein p+q is about 10. It should be noted that if the macromolecular antioxidant compositions of the present invention contain more than one compound of Structure II, each of the compounds can have the same or different constituents for R_1, R_2, R_5, and R_6, R and R', and each of the one or more compounds can have the same or different values for p and q.

[0033] The macromolecular antioxidant compositions of the present invention can contain one or more, or two or more, compounds represented by the following general structure:

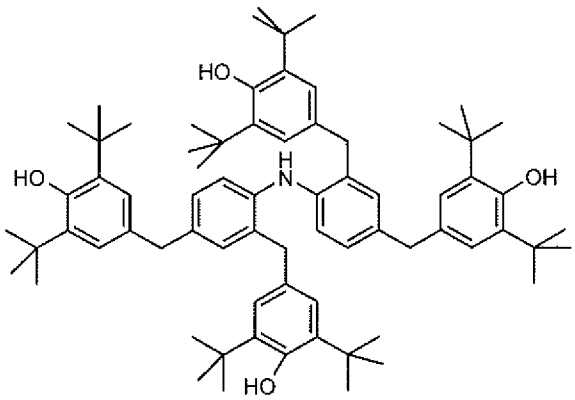


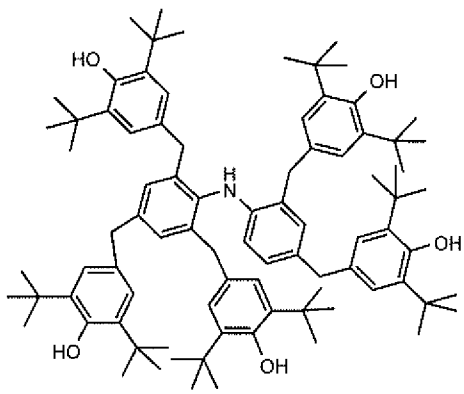
Structure III

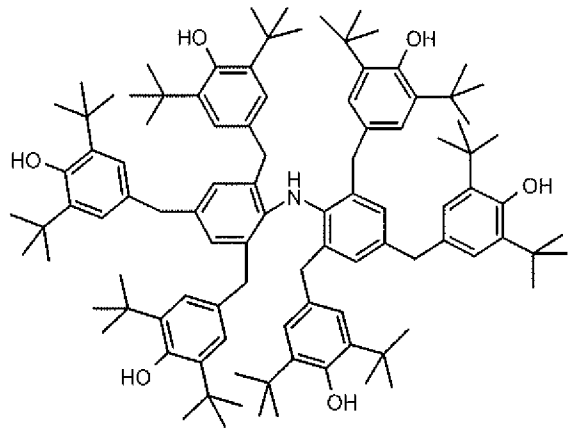
wherein R_1, R_2, R_5, R_6, R, R', are the same as described above, and p and q are whole numbers and p+q is in the range of from about 1 to about 12. It should be noted that if the macromolecular antioxidant compositions of the present invention contain more than one compound of Structure III, each of the compounds can have the same or different constituents for R_1, R_2, R_5, and R_6, R and R', and each of the one or more compounds can have the same or different values for p and q.

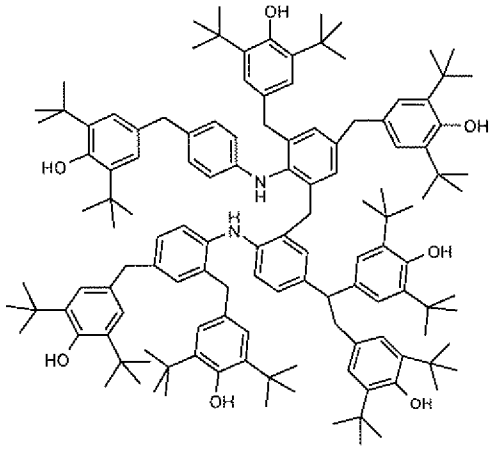
[0034] It is also known to those skilled in the art that the substitution pattern shown in Structures I, II, and III is for visual representation only and the alkyl and phenolic substitutions may take place on all the available active sites on the amine molecule.

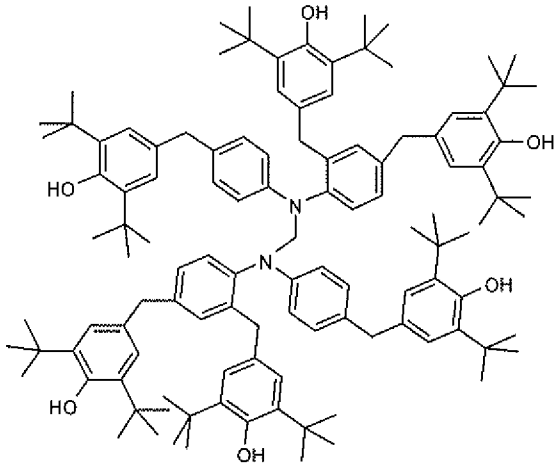
[0035] Some non-limiting examples of specific compounds represented by the above-described structures are:











[0036] The number or average number of 2,6-dihydrocarbyl-4-hydroxybenzyl groups in the macromolecular amine-phenolic antioxidant solids of this invention can vary depending upon the number of replaceable hydrogen atoms on the electron rich aromatic ring. For example, in the case of diphenylamine substituted only on one ring by a single branched chain alkyl group containing in the range of 3 to about 24 carbon atoms, the number of unsubstituted positions is nine while the number of activated positions in most cases is actually five, and thus the number of 2,6-dihydrocarbyl-4-hydroxybenzyl groups on the diphenylamine rings of macromolecular amine-phenolic antioxidant solids of this invention will typically be no greater than five.

EXAMPLES

[0037] The following example is illustrative of the principles of this invention. It is understood that this invention is not limited to any one specific embodiment exemplified herein, whether in the examples or the remainder of this patent application.

1. Crude 4-methoxymethyl-2-6-di-t-butylphenol was purified.
2. Into a 1 liter HASTELLOY C2000 autoclave was charged the following:
   24.0g of diphenylamine (0.14 moles);
   148g of 4-methoxymethyl-2,6-di-t-butylphenol (95.4 wt.% containing 1.5 wt.% 4-methoxymehtyl-2,6-di-t-butylphenol alcohol and 0.3 wt.% 4,4'-methylene-bis[2,6-di-t-butylphenol]; 4.0 equivalents 4-methoxymethyl-2,6-di-t-butylphenol when alcohol is included) that had been purified by flash operation;
   487g of methanol; and 1.25g of 98% H2SO4 (0.09 equivalents)
3. The autoclave was sealed and was then heated to about 80°C over 20 minutes
4. The contents of the autoclave were maintained near this temperature for an additional 5.4 hours before cooling to near room temperature.
5. A total of 651g of mother liquor was obtained of which 16g was precipitated into a large excess of water and then dried in a vacuum oven. The material contained 0.68 wt.% 4,4'-methylene-bis[2,6-di-t-butylphenol] and served as a control.
6. The remainder of the mother liquor was cofed along with 122g of water into a round bottom flask pre-charged with 685g of 80:20 MeOH:H2O w/w, 15.5g of NaOH, and 1.0g of (MAPAC) s seed crystals. The cofeed was conducted at about 40°C with vigorous mixing and lasted about 1.3 hours.
7. Once the MAPACs were precipitated, the resultant slurry was maintained at temperature for about 30 minutes and then filtered to recover the MAPACs solids.
8. The solids were slurry washed with 1034g of 80:20 methanol:water w/w and then plug flow washed with 1080g of 80:20 methanol:water w/w.
9. Afterwards the solids were plug flow washed with 995g of water containing a trace of sodium bicarbonate and finally with 1056g of pure water.
10. The wet solids were vacuum dried to afford 141g of dry MAPACs containing 0.33 wt.% 4,4'-methylene-bis[2,6-di-t-butylphenol], a relative reduction of 51% over the control mentioned above.

[0038] This invention is advantageous as it relates to the production of high purity macromolecular amine-phenolic compositions having oxidation inhibition characteristics that are exhibited when added to organic materials normally susceptible to oxidative degradation in the presence of air or oxygen, such as petroleum products, synthetic polymers, and elastomeric substances.

[0039] It is to be understood that the reactants and components referred to by chemical name or formula anywhere in the specification or claims hereof, whether referred to in the singular or plural, are identified as they exist prior to being combined with or coming into contact with another substance referred to by chemical name or chemical type (e.g., another reactant, a solvent, or etc.). It matters not what chemical changes, transformations and/or reactions, if any, take place in the resulting combination or solution or reaction medium as such changes, transformations and/or reactions are the natural result of bringing the specified reactants and/or components together under the conditions called for pursuant to this disclosure. Thus the reactants and components are identified as ingredients to be brought together in connection with performing a desired chemical reaction or in forming a combination to be used in conducting a desired reaction. Accordingly, even though the claims hereinafter may refer to substances, components and/or ingredients in the present tense ("comprises", "is", etc.), the reference is to the substance, component or ingredient as it existed at the time just before it was first contacted, combined, blended or mixed with one or more other substances, components and/or ingredients in accordance with the present disclosure. Whatever transformations, if any, which occur in situ as a reaction is conducted is what the claim is intended to cover. Thus the fact that a substance, component or ingredient may have lost its original identity through a chemical reaction or transformation during the course of contacting, combining, blending or mixing operations, if conducted in accordance with this disclosure and with the application of common sense and the ordinary skill of a chemist, is thus wholly immaterial for an accurate understanding and appreciation of the true meaning and substance of this disclosure and the claims thereof. As will be familiar to those skilled in the art, the terms "combined", "combining", and the like as used herein mean that the components that are "combined" or that one is "combining" are put into a container with each other. Likewise a "combination" of components means the components having been put together in a container.

[0040] While the present invention has been described in terms of one or more preferred embodiments, it is to be understood that other modifications may be made without departing from the scope of the invention, which is set forth in the claims below.

CLAIMS

1. A process comprising:
   A) heating a combination comprising an aromatic amine, an acid catalyst, an alkylating agent, and a solvent to about 35°C to about 250°C, thereby forming a reaction solution comprising one or more macromolecular amine-phenolic antioxidant solids and one or more non-macromolecular byproducts;
   B) combining at least the reaction solution and an antisolvent such that a precipitant comprising a substantial portion of the macromolecular amine-phenolic antioxidant solids precipitates out of the reaction solution, while a substantial portion of the non-macromolecular byproducts remain in the reaction solution;
   C) separating the precipitant from the reaction solution; and
   D) drying the precipitant to produce a MAPAC comprising less than about 1 wt.% non-macromolecular byproducts.

2. A process according to claim 1 wherein the aromatic amine comprises diphenylamine, phenynaphthylamine, dinaphthylamine, phenyltolylamine, di-tolyl amine, tolylnaphthylamine, hydrocarbyl substituted diphenylamine, hydrocarbyl substituted phenylnaphthylamine, hydrocarbyl substituted dinaphthylamine, N-methyl diphenylamine, N-ethyl diphenylamine, N-propyl diphenylamine, N-butyl diphenylamine, triphenylamine, N-methyl phenylnaphthylamine, N-ethyl phenylnaphthylamine, N-propyl phenylnaphthylamine, or N-butyl phenylnaphthylamine.

3. A process according to claim 1 wherein the acid catalyst comprises sulphuric acid or methanesulfonic acid.

4. A process according to claim 1 wherein the alkylating agent comprises 4-methoxymethyl-2,6-di-t-butylphenol, 4-hydroxymethyl-2,6-di-t-butylphenol, or 4-acetoxymethyl-2,6-di-t-butylphenol.

5. A process according to claim 1 wherein the solvent comprises alcohol or a carboxylic acid.

6. A process according to claim 1 wherein the antisolvent comprises water.

7. A process according to claim 1 wherein the wherein B) is replaced with:

B) combining at least the reaction solution, an antisolvent, and a strong base such that a precipitant comprising a substantial portion of the macromolecular amine-phenolic antioxidant solids precipitates out of the reaction solution, while a substantial portion of the non-macromolecular byproducts remain in the reaction solution;

8. A process according to claim 7 wherein the strong base comprises sodium hydroxide or potassium hydroxide.

9. A process according to claim 1 wherein the alkylating agent has been purified by crystallization, distillation, flashing, or washing.

10. A process comprising:

A) purifying a 4-substituted-2,6-di-t-butylphenol to reduce the amount of non-macromolecular impurities to less than about 5 wt%;

B) heating a combination comprising the purified 4-substituted-2,6-di-t-butylphenol diphenylamine, an acid catalyst, and an alcohol to about 40°C to about 250°C, thereby forming a reaction solution comprising one or more macromolecular amine-phenolic antioxidant solids and one or more non-macromolecular byproducts;

C) combining at least the reaction solution and an antisolvent such that a precipitant comprising a substantial portion of the macromolecular amine-phenolic antioxidant solids precipitates out of the reaction solution, while a substantial portion of the non-macromolecular byproducts remain in the reaction solution;

D) separating the precipitant from the reaction solution; and

E) drying the precipitant to produce a MAPAC comprising less than about 1 wt.% non-macromolecular byproducts.

11. A MAPAC comprising less than about 1 wt.% non-macromolecular byproducts.

12. A MAPAC comprising less than about 1 wt.% non-macromolecular byproducts, said MAPAC having been produced by:

A) heating a combination comprising an aromatic amine, an acid catalyst, an alkylating agent, and a solvent to about 35°C to about 250°C, thereby forming a reaction solution comprising one or more macromolecular amine-phenolic antioxidant solids and one or more non-macromolecular byproducts;

B) combining at least the reaction solution and an antisolvent such that a precipitant comprising a substantial portion of the macromolecular amine-phenolic antioxidant solids precipitates out of the reaction solution, while a substantial portion of the non-macromolecular byproducts remain in the reaction solution;

C) separating the precipitant from the reaction solution; and

D) drying the precipitant to produce the MAPAC.

13. A MAPAC comprising less than about 1 wt. % 4,4'-methylene-bis(2,6-di-tert-butylphenol).

14. A composition comprising a base oil and a MAPAC containing less than about 1 wt. % 4,4'-methylene-bis(2,6-di-tert-butylphenol).

15. A polymer composition comprising a MAPAC containing less than about 1 wt. % 4,4'-methylene-bis(2,6-di-tert-butylphenol).

16. A lubricant composition comprising a MAPAC containing less than about 1 wt. % 4,4'-methylene-bis(2,6-di-tert-butylphenol).

17. An engine oil composition comprising a MAPAC containing less than about 1 wt. % 4,4'-methylene-bis(2,6-di-tert-butylphenol).

18. An industrial oil composition comprising a MAPAC containing less than about 1 wt. % 4,4'-methylene-bis(2,6-di-tert-butylphenol).

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2010/021035

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07C213/08 C07C213/10 C07C215/74 C08K5/13 C10M165/00

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)
C07C C08K C10M

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 practical, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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X	WO 2008/048987 A1 (ALBEMARLE CORP [US]; SABAHI MAHMOOD [US]) 24 April 2008 (2008-04-24) cited in the application	11-18
A	paragraph [0002] claims 1-19; examples 3,4	1-10
X	WO 2008/048990 A2 (ALBEMARLE CORP [US]; SABAHI MAHMOOD [US]; GATTO VINCENT J [US]; ELNAGA) 24 April 2008 (2008-04-24) cited in the application	11-18
A	paragraph [0002] claims 1-23; examples 2-6	1-10
X	WO 2008/048989 A2 (ALBEMARLE CORP [US]; SABAHI MAHMOOD [US]; GATTO VINCENT J [US]; ELNAGA) 24 April 2008 (2008-04-24) cited in the application	11-18
A	paragraph [0002]; claims 1-25	1-10

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

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"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
12 March 2010	19/03/2010

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, Fax: (+31-70) 340-3016	Scheid, Günther

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2010/021035

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