

1 **PROCESS FOR MAKING GROUP II METAL**
2 **OVERBASED SULFURIZED ALKYLPHENOLS**

3 FIELD OF THE INVENTION

4 This invention is directed to a novel process for making Group II metal
5 overbased sulfurized alkylphenols, which process uses ethylene carbonate as
6 both a source of carbon dioxide and ethylene glycol. In particular, under the
7 reaction conditions using ethylene carbonate, carbonation time is reduced to
8 one quarter or less than time taught in the prior art to make Group II metal
9 overbased sulfurized alkylphenol compositions. The present invention is also
10 directed to a detergent-dispersant additive composition comprising Group II
11 metal overbased sulfurized alkylphenols; wherein the Group II metal
12 overbased sulfurized alkylphenols have a color of 3.5 or lower, as measured
13 using ASTM Test No. D 6045, and increased hydrolytic stability as measured
14 by a modified ASTM Test No. 2619, wherein the TBN of the Group II metal
15 overbased sulfurized alkylphenols decreases less than 10 percent, and
16 preferably less than 8 percent, after the addition of 2.0 percent water and after
17 6 days at 80°C. The present invention is also directed to a process using
18 ethylene carbonate or alkyl-substituted ethylene carbonate and water for
19 delivering in situ equimolar quantities of ethylene glycol and carbon dioxide for
20 use as reactants in chemical reactions.

21 BACKGROUND OF THE INVENTION

22 The operation of diesel and spark ignition internal combustion engines is
23 typically accompanied by the formation of sludge, lacquer and resinous
24 deposits which adhere to the moving engine parts and thereby reduce engine
25 efficiency. In order to prevent or reduce the formation of these deposits, a
26 wide variety of chemical additives have been developed for incorporation into
27 lubricating oils. These additives are commonly referred to as detergents and
28 dispersants. Dispersants have the ability to keep deposit forming materials

1 suspended in the oil so as to retard deposit formation during engine operation.
2 Detergents have the ability to remove preexisting deposits from the engine
3 during engine operation and to neutralize acids in railroad, marine and
4 automotive engines.

5 Among the many additives which have been developed for this purpose,
6 Group II metal overbased sulfurized alkylphenol compositions have been
7 found to be highly effective detergent/dispersants for use in lubricating oils.
8 Furthermore, these additives are excellent oxidation and corrosion inhibitors
9 and, by virtue of their alkalinity reserve, have the ability to neutralize acidic
10 combustion and oxidation products. Such acidic products form during engine
11 operation, particularly when operated on high sulfur containing fuels, and tend
12 to accumulate in the lubricating oil. The sulfur in these compositions has
13 antioxidant activity.

14 The ability of Group II metal overbased sulfurized alkylphenol compositions to
15 neutralize such acidic products can be directly measured by determining the
16 total base number (TBN) of the composition. Higher TBNs reflect a greater
17 capacity for these compositions to neutralize acids generated during engine
18 operation. The term "overbased" is used to describe those sulfurized alkaline
19 earth metal alkylphenates in which the ratio of the number of equivalents of
20 the alkaline earth metal moiety to the number of equivalents of the phenol
21 moiety is greater than one, and is usually greater than 1.2 and may be as high
22 as 4.5 or greater. In contrast, the equivalent ratio of alkaline earth metal
23 moiety to phenol moiety in "neutral" alkaline earth metal sulfurized alkylphenol
24 is 1. Thus, the "overbased" material typically contains greater than 20% in
25 excess of the alkaline earth metal present in the corresponding "neutral"
26 material. For this reason, "overbased" alkaline earth metal sulfurized
27 alkylphenol has a greater capability for neutralizing acidic matter than does
28 the corresponding "neutral" alkaline earth metal sulfurized alkylphenol.

1 The preparation of Group II metal overbased sulfurized alkylphenate
2 compositions is well known in the art. A number of patents have discussed
3 processes in which overbasing is accomplished by the direct addition of
4 ethylene glycol and carbon dioxide.

5 For example, U.S. Pat. No. 3,178,368 discloses the basic process for making
6 metal overbased alkylphenates using an alkylphenol, a sulfonate, a high
7 molecular weight alcohol, lubricating oil, sulfur, hydrated lime (or calcium
8 oxide), ethylene glycol and carbon dioxide. The metal overbased sulfurized
9 alkylphenates prepared by this process have greater than 20% metal
10 compared to the neutral alkylphenates.

11 U. S. Pat. No. 3,367,867 discloses the preparation of low-foaming metal
12 overbased alkylphenates by starting with alkylphenols wherein the alkyl group
13 is a mixture of straight and branched chain alkyl groups.

14 U.S. Pat. No. 3,801,507 discloses sulfurized metal alkylphenates that have a
15 ratio of sulfur to calcium between 1 and 2 which provides for better
16 dispersancy and improved antioxidant activity.

17 U.S. Pat. No. 4,251,379 discloses a process for increasing the TBN of metal
18 overbased sulfurized alkylphenates to more than 250.

19 U.S. Pat. No. 4,744,921 discloses the use of a sulfurization catalyst in the
20 preparation of metal overbased sulfurized alkylphenates to obtain products
21 having a lower crude sediment and TBN greater than 300.

22 U.S. Pat. No. 5,320,762 discloses the use of alkylphenols having a
23 substantially straight chain alkyl substituent attached to the phenol ring in a
24 middle position to obtain metal overbased sulfurized alkylphenates which
25 possess low viscosity at high TBNs.

1 U.S. Pat. Nos. 5,714,443 and 5,716,914 disclose the preparation and use of
2 metal overbased sulfurized alkylphenates modified by incorporation of a
3 mono-carboxylic acid or a di- or polycarboxylic acid in lubricating oils. Also
4 disclosed is the use of a metal halide catalyst to increase the TBN in the metal
5 overbased sulfurized alkylphenate product.

6 European Patent No. 259974 discloses a process for the preparation of
7 Group II overbased sulfurized alkylphenols characterized as possessing a
8 TBN of 300 or greater and having viscosities less than 1000 cSt at 100°C. In
9 particular. This patent teaches that the hydrolytic stability of the overbased
10 sulfurized alkylphenols is improved by the use of a sulfurization catalyst, such
11 as 2-mercaptobenzothiozole and derivatives thereof.

12 European Patent No. 989178 discloses a process for the preparation of an
13 overbased alkaline earth metal phenate sulfide having a high base number
14 and good hydrolytic stability.

15 U.S. Pat. No. 4,465,603 discloses the replacement of the ethylene glycol
16 employed in the overbasing step in the preparation of metal overbased
17 sulfurized alkylphenates with dimethyl carbonate. It is believed that the
18 hydrolysis products of dimethyl carbonate are likely carbon dioxide and methyl
19 alcohol.

20 Typically, Group II metal overbased sulfurized alkylphenol compositions are
21 prepared by treating alkylphenol in a suitable diluent (e.g., a lubricating oil)
22 with an amount of an alkaline earth metal hydroxide, oxide and/or alkoxide in
23 excess of that necessary to neutralize the phenol and then sulfurizing the
24 resulting product, optionally in the presence of a sulfurizing catalyst. The
25 sulfurized product is then treated with carbon dioxide to provide the Group II
26 metal overbased sulfurized alkylphenol composition.

1 Such Group II metal overbased sulfurized alkylphenols are useful for
2 preparing additive compositions which are further used to prepare a fully
3 formulated lubricant composition suitable for use in an internal combustion
4 engine. Typically, the additive composition is prepared as a concentrate and
5 is then shipped to a point where it is used to prepare fully formulated lubricant
6 compositions by combining requisite amounts of several additive
7 compositions, including a Group II metal overbased sulfurized alkylphenol
8 composition, to a base stock.

9 In order to reduce shipping costs, the Group II metal overbased sulfurized
10 alkylphenol is preferably prepared to contain as little diluent as possible.
11 Additionally, in order to achieve the maximum amount of acid neutralization
12 possible, the Group II metal overbased sulfurized alkylphenol is preferably
13 prepared to contain as high a TBN as possible.

14 Thus, while Group II metal overbased sulfurized alkylphenols produced in the
15 prior art are reported to possess TBNs of up to about 350 or more, in practice,
16 commercial Group II metal overbased sulfurized alkylphenols typically have a
17 TBN of less than about 300, and more typically less than about 275, so as to
18 ensure that the composition possesses acceptable viscosity because viscosity
19 typically increases with an increase in the TBN. In view of the above, it is
20 generally desirable to increase the TBN of the Group II metal overbased
21 sulfurized alkylphenols.

22 The chemistry in the conventional preparation of overbased sulfurized
23 alkylphenols begins with the reaction of lime (calcium hydroxide) and the
24 alkylphenol to form calcium phenate with the aid of ethylene glycol as a
25 promoter. This reaction typically begins at approximately 135°C, with the
26 generation of water. The calcium phenate quickly reacts with sulfur in a
27 reaction that cross-links the alkylphenol aromatic rings. At this point, the
28 reaction is ready for carbonation.

29

1 The conventional carbonation process uses carbon dioxide and ethylene
2 glycol for the preparation of overbased sulfurized alkylphenols. The key
3 change in the present process is the replacement of the carbon
4 dioxide/ethylene glycol carbonation process with a simpler and faster ethylene
5 carbonate process. Ethylene carbonate serves as a source of equal molar
6 quantities of carbon dioxide and ethylene glycol through hydrolysis.
7
8 Optimization of processing properties for highly overbased sulfurized
9 alkylphenols is highly empirical, owing to the high degree of overbasing which
10 causes the overbased sulfurized phenol compositions to be less stable and,
11 accordingly, more susceptible to degradation. Carbonation of sulfurized
12 alkylphenols by the prior art process is the most time consuming processing
13 step for production of overbased sulfurized alkylphenols. This is because
14 gaseous carbon dioxide must be added carefully and slowly at the right
15 temperature. For example, if carbon dioxide is charged too rapidly, a portion
16 of the gas can simply escape through the reactor to the atmosphere or vent.
17 In such a case, insufficient carbon dioxide will ultimately be delivered to the
18 reactor resulting in high crude sediment. Fundamentally, this is an issue of
19 mixing and reaction rate, because the gaseous carbon dioxide must be added
20 to the reactor at temperatures far above the boiling point. A further
21 complication may arise if the carbon dioxide is inadequately dispersed in the
22 reaction mixture. This can occur if the reactor does not have sufficient
23 agitation relative to the rate of gas introduction. Inadequate agitation can
24 result in "local over-carbonation" which can result in poor product performance
25 such as hydrolytic stability.
26
27 Overbased sulfurized alkylphenol carbonation is a complex process and is
28 highly dependent on reaction conditions. The reactions involved are subtle
29 and not perfectly understood. For example, glycol plays a critical role in this
30 process and the overbased sulfurized alkylphenol undergoes oxidation with
31 subsequent condensation of the reaction intermediates.

1 The use of ethylene carbonate in the carbonation process of the present
2 invention is advantageous because it eliminates the problems of timing the
3 addition of carbon dioxide, adequately dispersing it, and correctly charging the
4 ethylene glycol. This is because the hydrolysis of ethylene carbonate to
5 ethylene glycol and carbon dioxide occurs in situ which results in the carbon
6 dioxide produced to be completely dispersed in the reaction medium.

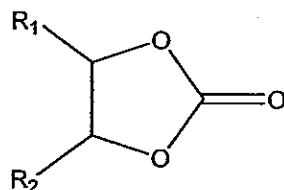
7 It is believed that the present rapid carbonation process for overbasing
8 sulfurized alkylphenols using ethylene carbonate instead of ethylene glycol
9 and carbon dioxide can also be used for the preparation of highly overbased
10 alkyl aromatic salicylic acid, sulfurized alkyl aromatic salicylic acid, and alkyl
11 aromatic sulfonic acid and mixtures thereof with advantages similar to those
12 observed for the preparation of overbased sulfurized alkyl phenol
13 compositions.

14 SUMMARY OF THE INVENTION

15 The present invention is directed toward a process for preparing Group II
16 metal overbased sulfurized alkylphenols. The present invention is also
17 directed to a detergent-dispersant additive composition comprising Group II
18 metal overbased sulfurized alkylphenols, wherein the Group II metal
19 overbased sulfurized alkylphenols have a color of 3.5 or lower, as measured
20 by ASTM Test No. D 6045. The Group II metal overbased sulfurized
21 alkylphenols also have increased hydrolytic stability as measured by a
22 modified ASTM Test No. 2619, wherein the TBN of the Group II metal
23 overbased sulfurized alkylphenols decreases less than 10 percent, and
24 preferably less than 8 percent, after the addition of 2.0 percent water and after
25 6 days at 80°C. The present invention is also directed to a process using
26 ethylene carbonate or alkyl-substituted ethylene carbonate and water for
27 delivering in situ equimolar quantities of ethylene glycol and carbon dioxide for
28 use as reactants in chemical reactions.

1 In particular, the process of the present invention for preparing Group II metal
2 overbased sulfurized alkylphenols comprises:

3
4 forming a reaction mixture by combining a sulfurized alkylphenol wherein the
5 alkyl group contains a sufficient number of carbon atoms to render oil-soluble
6 the resulting Group II metal overbased sulfurized alkylphenol, an alkanol
7 containing about 6 to about 15 carbon atoms, a Group II metal oxide,
8 hydroxide or C₁-C₆ alkoxide, a C₂-C₁₀ alkylene glycol and with an alkylene
9 carbonate selected from ethylene carbonate or a mono-alkyl or di-alkyl
10 substituted ethylene carbonate, said alkylene carbonate having the following
11 structure:



13 wherein R₁ and R₂ are independently hydrogen or alkyl containing one to
14 three carbon atoms; and wherein the contacting is carried out for a time and
15 at a temperature sufficient to form in situ carbon dioxide and alkylene glycol,
16 or a reacting equivalent, to form a product comprising a Group II earth metal
17 overbased sulfurized alkylphenol.

18 In the alkylene carbonate structure above, preferably one of R₁ and R₂ is
19 hydrogen and the other is hydrogen or methyl. In other words, the alkylene
20 carbonate is preferably ethylene carbonate or propylene carbonate. More
21 preferably, R₁ and R₂ are both hydrogen; that is, the alkylene carbonate is
22 ethylene carbonate.

23 The sulfurized alkylphenol in the reaction mixture of the present process may
24 be replaced with a Group II metal sulfurized alkylphenate.

1 The reaction mixture of the present process further comprises an oil-soluble
2 Group II metal overbased natural or synthetic hydrocarbyl sulfonic acid,
3 sulfonate, or mixtures thereof.

4 The alkylene carbonate is added to the reaction mixture over a time period of
5 about 5 minutes to about 120 minutes, preferably the alkylene carbonate is
6 added to the reaction mixture over a time period of about 15 minutes to about
7 90 minutes, and more preferably the alkylene carbonate is added to the
8 reaction mixture over a time period of about 30 minutes to about 60 minutes.

9 The process of the present invention is typically conducted at about 150°C to
10 about 215°C, preferably conducted at from about 160°C to about 200°C, and
11 more preferably conducted at from about 170°C to about 190°C.

12 The alkyl group of the mono-alkyl or di-alkyl substituted ethylene carbonate
13 useful for carrying out the process of the present invention is preferably a
14 mono-substituted methyl group, i.e., the alkylene carbonate is propylene
15 carbonate. Most preferably, the alkylene carbonate is ethylene carbonate.

16 The alkyl group of the alkylphenol and the alkyl phenate employed in the
17 process of the instant invention contains a sufficient number of carbon atoms
18 to render the Group II metal overbased sulfurized alkylphenol oil-soluble. In
19 general, alkyl groups of about 8 carbon atoms or more are sufficient to render
20 the Group II metal overbased sulfurized alkylphenol oil-soluble.

21 Furthermore, in a preferred embodiment, the alkyl group of the alkylphenol
22 and the alkyl phenate is attached predominantly at the para position of the
23 phenol ring. Preferably, the alkylphenol and the alkyl phenate containing the
24 para attachment of the alkyl group is from about 75 to about 95 weight
25 percent of the total alkylphenol and the alkyl phenate. More preferably, the
26 alkylphenol and the alkyl phenate containing the para attachment of the alkyl

1 group is from about 80 to about 95 weight percent of the total alkylphenol and
2 the alkyl phenate.

3

4 In one preferred embodiment, the alkyl group of said alkylphenol and the alkyl
5 phenate contains from 25 to 100 mole percent predominantly straight-chain
6 alkyl groups of from 15 to 35 carbon atoms and from 75 to 0 mole percent of
7 the alkyl groups are branched-chain, such as polypropenyl, of from 9 to
8 18 carbon atoms. More preferably, the alkyl group of said alkylphenol and the
9 alkyl phenate contains from 35 to 100 mole percent predominantly
10 straight-chain alkyl groups of from 15 to 35 carbon atoms and from 65 to
11 0 mole percent of the alkyl groups are branched-chain, such as polypropenyl,
12 of from 9 to 18 carbon atoms. In yet another preferred embodiment, the alkyl
13 group of said alkylphenol and the alkyl phenate contains from 40 to 70 mole
14 percent predominantly straight-chain alkyl groups of from 15 to 35 carbon
15 atoms and from 60 to 30 mole percent of the alkyl groups are branched-chain,
16 such as polypropenyl, of from 9 to 18 carbon atoms. Most preferably, the
17 alkyl group of said alkylphenol and the alkyl phenate contains approximately
18 50 mole percent predominantly straight-chain alkyl groups of from 15 to
19 35 carbon atoms and approximately 50 mole percent of the alkyl groups are
20 branched-chain, such as polypropenyl, of from 9 to 18 carbon atoms.

21

22 The preferred oil-soluble Group II metal overbased natural or synthetic
23 hydrocarbyl sulfonic acid, sulfonate, or mixture thereof useful for the process
24 of the present invention are single-ring alkyl aromatic hydrocarbyl sulfonic
25 acid, sulfonate, or mixture thereof, more preferred are alkylbenzene or
26 alkyltoluene sulfonic acids, sulfonates or mixtures thereof. The alkyl group on
27 the aromatic ring can be from about 6 to about 60 carbon atoms. Preferably,
28 the alkyl group is from about 10 to about 40 carbon atoms and most
29 preferably from about 20 to about 28 carbon atoms.

30

31 In the process of the present invention, the Group II metal oxide, hydroxide or
32 C₁-C₆ alkoxide is selected from the group consisting of calcium, barium,

1 magnesium and strontium oxide, hydroxide or C₁-C₆ alkoxide and mixtures
2 thereof. Preferably, the Group II metal oxide, hydroxide or C₁-C₆ alkoxide is
3 Dolomite comprising Ca(OH)₂.Mg(OH)₂. Most preferably, the Group II metal
4 oxide, hydroxide or C₁-C₆ alkoxide is calcium hydroxide.

5
6 As used herein, the term "Group II metal" means calcium, barium,
7 magnesium, and strontium. Preferably, the Group II metal is selected from
8 the group consisting of calcium, magnesium, barium, and mixtures thereof.
9 Most preferably, the Group II metal is calcium.

10
11 In the present process, the alkanol contains at least 6 carbon atoms, and
12 typically from about 8 to about 13 carbon atoms. Preferably, the alkanol is
13 isodecyl alcohol.

14
15 An optional step of the process of the present invention comprises heating the
16 reaction mixture under reduced pressure to remove a portion of the unreacted
17 C₂-C₁₀ alkylene glycol and carbon dioxide. This step is preferably conducted
18 at a temperature sufficient to effect removal of a portion of the water in the
19 reaction system without additionally removing significant amounts, i.e., greater
20 than about 15%, of either the alkanol containing 6 to 18 carbon atoms and the
21 C₂-C₁₀ alkylene glycol. This step is typically conducted at from about 175°C to
22 about 220°C, and preferably conducted at from about 200°C to about 215°C.

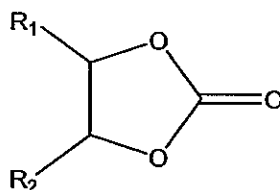
23
24 The C₂-C₁₀ alkylene glycol of the present process is preferably ethylene
25 glycol.

26
27 An alternate embodiment of the present process for preparing Group II metal
28 overbased sulfurized alkylphenols comprises the steps of:

29
30 (a) forming a reaction mixture by combining a sulfurized alkylphenol wherein
31 the alkyl group contains a sufficient number of carbon atoms to render
32 oil-soluble the resulting Group II metal overbased sulfurized alkylphenol,

1 an alkanol containing about 6 to about 15 carbon atoms, a Group II
2 metal oxide, hydroxide or C₁-C₆ alkoxide, and a C₂-C₁₀ alkylene glycol;
3 and

4 (b) contacting said reaction mixture with an alkylene carbonate selected
5 from ethylene carbonate or a mono-alkyl or di-alkyl substituted ethylene
6 carbonate, said alkylene carbonate having the following structure:



8 wherein R₁ and R₂ are independently hydrogen or alkyl containing one to
9 three carbon atoms; and wherein the contacting is carried out for a time
10 and at a temperature sufficient to form in situ carbon dioxide and
11 alkylene glycol, or a reacting equivalent, to form a product comprising a
12 Group II earth metal overbased sulfurized alkylphenol.

13 In the alkylene carbonate structure above, preferably one of R₁ and R₂ is
14 hydrogen and the other is hydrogen or methyl. In other words, the alkylene
15 carbonate is preferably ethylene carbonate or propylene carbonate. More
16 preferably, R₁ and R₂ are both hydrogen; that is, the alkylene carbonate is
17 ethylene carbonate.

18 The sulfurized alkylphenol in the reaction mixture of the present process may
19 be replaced with a Group II metal sulfurized alkylphenate.

20 The reaction mixture of the present process further comprises an oil-soluble
21 Group II metal overbased natural or synthetic hydrocarbyl sulfonic acid,
22 sulfonate, or mixtures thereof.

1 The alkylene carbonate is added to the reaction mixture over a time period of
2 about 5 minutes to about 120 minutes, preferably the alkylene carbonate is
3 added to the reaction mixture over a time period of about 15 minutes to about
4 90 minutes, and more preferably the alkylene carbonate is added to the
5 reaction mixture over a time period of about 30 minutes to about 60 minutes.

6 Step (b) is typically conducted at about 150°C to about 215°C, preferably
7 conducted at from about 160°C to about 200°C, and more preferably
8 conducted at from about 170°C to about 190°C.

9 The alkyl group of the mono-alkyl or di-alkyl substituted ethylene carbonate
10 useful for carrying out the process of the present invention is preferably a
11 mono-substituted methyl group, i.e., the alkylene carbonate is propylene
12 carbonate. Most preferably, the alkylene carbonate is ethylene carbonate.

13 The alkyl group of the alkylphenol and the alkyl phenate employed in the
14 process of the instant invention contains a sufficient number of carbon atoms
15 to render the Group II metal overbased sulfurized alkylphenol oil-soluble. In
16 general, alkyl groups of about 8 carbon atoms or more are sufficient to render
17 the Group II metal overbased sulfurized alkylphenol oil-soluble.

18

19 Furthermore, in a preferred embodiment, the alkyl group of the alkylphenol
20 and the alkyl phenate is attached predominantly at the para position of the
21 phenol ring. Preferably, the alkylphenol and the alkyl phenate containing the
22 para attachment of the alkyl group is from about 75 to about 95 weight
23 percent of the total alkylphenol and the alkyl phenate. More preferably, the
24 alkylphenol and the alkyl phenate containing the para attachment of the alkyl
25 group is from about 80 to about 95 weight percent of the total alkylphenol and
26 the alkyl phenate.

27

28 In one preferred embodiment, the alkyl group of said alkylphenol and the alkyl
29 phenate contains from 25 to 100 mole percent predominantly straight-chain

1 alkyl groups of from 15 to 35 carbon atoms and from 75 to 0 mole percent of
2 the alkyl groups are branched-chain, such as polypropenyl, of from 9 to 18
3 carbon atoms. More preferably, the alkyl group of said alkylphenol and the
4 alkyl phenate contains from 35 to 100 mole percent predominantly
5 straight-chain alkyl groups of from 15 to 35 carbon atoms and from 65 to
6 0 mole percent of the alkyl groups are branched-chain, such as polypropenyl,
7 of from 9 to 18 carbon atoms. In yet another preferred embodiment, the alkyl
8 group of said alkylphenol and the alkyl phenate contains from 40 to 70 mole
9 percent predominantly straight-chain alkyl groups of from 15 to 35 carbon
10 atoms and from 60 to 30 mole percent of the alkyl groups are branched-chain,
11 such as polypropenyl, of from 9 to 18 carbon atoms. Most preferably, the
12 alkyl group of said alkylphenol and the alkyl phenate contains approximately
13 50 mole percent predominantly straight-chain alkyl groups of from 15 to
14 35 carbon atoms and approximately 50 mole percent of the alkyl groups are
15 branched-chain, such as polypropenyl, of from 9 to 18 carbon atoms.

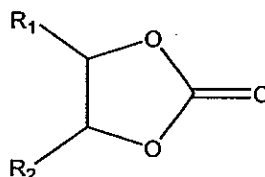
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17 The preferred oil-soluble Group II metal overbased natural or synthetic
18 hydrocarbyl sulfonic acid, sulfonate, or mixture thereof useful for the process
19 of the present invention are single-ring alkyl aromatic hydrocarbyl sulfonic
20 acid, sulfonate, or mixture thereof, more preferred are alkylbenzene or
21 alkyltoluene sulfonic acids, sulfonates or mixtures thereof. The alkyl group on
22 the aromatic ring can be from about 6 to about 60 carbon atoms. Preferably,
23 the alkyl group is from about 10 to about 40 carbon atoms and most
24 preferably from about 20 to about 28 carbon atoms.

25
26 In the process of the present invention, the Group II metal oxide, hydroxide or
27 C₁-C₆ alkoxide is selected from the group consisting of calcium, barium,
28 magnesium and strontium oxide, hydroxide or C₁-C₆ alkoxide and mixtures
29 thereof. Preferably, the Group II metal oxide, hydroxide or C₁-C₆ alkoxide is
30 Dolomite comprising Ca(OH)₂.Mg(OH)₂. Most preferably, the Group II metal
31 oxide, hydroxide or C₁-C₆ alkoxide is calcium hydroxide.

32

1 As used herein, the term "Group II metal" means calcium, barium,
2 magnesium, and strontium. Preferably, the Group II metal is selected from
3 the group consisting of calcium, magnesium, barium, and mixtures thereof.
4 Most preferably, the Group II metal is calcium.
5
6 In the present process, the alkanol contains at least 6 carbon atoms, and
7 typically from about 8 to about 13 carbon atoms. Preferably, the alkanol is
8 isodecyl alcohol.
9
10 An optional step of the process of the present invention comprises heating the
11 reaction mixture under reduced pressure to remove a portion of the unreacted
12 C₂-C₁₀ alkylene glycol and carbon dioxide. This step is preferably conducted
13 at a temperature sufficient to effect removal of a portion of the water in the
14 reaction system without additionally removing significant amounts, i.e., greater
15 than about 15%, of either the alkanol containing 6 to 18 carbon atoms and the
16 C₂-C₁₀ alkylene glycol. This step is typically conducted at from about 175°C to
17 about 220°C, and preferably conducted at from about 200°C to about 215°C.
18
19 The C₂-C₁₀ alkylene glycol of the present process is preferably ethylene
20 glycol.
21
22 Another alternate embodiment of the process of the present invention
23 comprises the steps of:
24
25 (a) forming a first reaction mixture by combining an alkylphenol wherein the
26 alkyl group contains a sufficient number of carbon atoms to render
27 oil-soluble the resulting Group II metal overbased sulfurized alkylphenol,
28 an oil-soluble Group II metal overbased natural or synthetic hydrocarbyl
29 sulfonic acid, sulfonate, or mixtures thereof, and an alkanol containing
30 about 6 to about 18 carbon atoms, the temperature of said first reaction
31 mixture being at least about 40°C;
32

- (b) contacting said first reaction mixture with a second reaction mixture comprising a Group II metal oxide, hydroxide or C₁-C₆ alkoxide; a sulfurization agent and an inert hydrocarbon diluent at a temperature and for a time sufficient to effect sulfurization of the alkylphenol to form a third reaction mixture;
- (c) contacting said third reaction mixture with a C₂-C₁₀ alkylene glycol to form a fourth reaction mixture; and
- (d) contacting said fourth reaction mixture with an alkylene carbonate selected from ethylene carbonate or a mono-alkyl or di-alkyl substituted ethylene carbonate, wherein the alkylene carbonate has the following formula:



wherein R₁ and R₂ are independently hydrogen or alkyl containing one to three carbon atoms; and wherein said contacting is carried out for a time and at a temperature sufficient to form in situ carbon dioxide and alkylene glycol, or a reacting equivalent, to form a product comprising a Group II earth metal overbased sulfurized alkylphenol.

In step (c), after contacting the third reaction mixture with a C₂-C₁₀ alkylene glycol, the temperature of the system is preferably raised, if necessary, from that of step (b) to between about 120°C and about 190°C. Also in step (c), the C₂-C₁₀ alkylene glycol addition is preferably conducted at from about 100°C to about 190°C, and even more preferably at from 125°C to 165°C.

1 In step (d), the temperature is maintained below about 215°C and the
2 ethylene carbonate is added to the fourth reaction mixture over a time period
3 of about 5 minutes to about 120 minutes, preferably over a time period of
4 about 15 minutes to about 90 minutes, and more preferably over a time period
5 of about 30 minutes to about 60 minutes.

6

7 Step (d) is typically conducted at about 150°C to about 215°C, preferably
8 conducted at from about 160°C to about 200°C, and more preferably
9 conducted at from about 170°C to about 190°C.

10 In the alkylene carbonate structure above, preferably one of R₁ and R₂ is
11 hydrogen and the other is hydrogen or methyl. In other words, the alkylene
12 carbonate is preferably ethylene carbonate or propylene carbonate. More
13 preferably, R₁ and R₂ are both hydrogen; that is, the alkylene carbonate is
14 ethylene carbonate.

15 An optional step (e) comprises heating the fourth reaction mixture of step (d)
16 under reduced pressure to remove a portion of the unreacted C₂-C₁₀ alkylene
17 glycol and carbon dioxide. Step (e) is preferably conducted at a temperature
18 sufficient to effect removal of a portion of the water in the reaction system
19 without additionally removing significant amounts, i.e., greater than about
20 15%, of either the alkanol containing 6 to 18 carbon atoms and the C₂-C₁₀
21 alkylene glycol. Step (e) is typically conducted at from about 175°C to about
22 220°C, and preferably conducted at from about 200°C to about 215°C.

23

24 This embodiment of the process of the present invention further optionally
25 comprises in step (a) or in step (b), or in both steps (a) and (b), a sulfurization
26 catalyst, wherein the sulfurization catalyst is preferably a hydrogen halide, an
27 ammonium halide, a metal halide or 2-mercaptobenzothiozole. More
28 preferably, the catalyst is a metal halide, and even more preferably calcium
29 chloride.

30

1 The alkyl group of the alkylphenol employed in the process of the instant
2 invention contains a sufficient number of carbon atoms to render the Group II
3 metal overbased sulfurized alkylphenol oil-soluble. In general, alkyl groups of
4 about 8 carbon atoms or more are sufficient to render the Group II metal
5 overbased sulfurized alkylphenol oil-soluble.

6
7 Furthermore, in a preferred embodiment, the alkyl group of the alkylphenol is
8 attached predominantly at the para position of the phenol ring. Preferably, the
9 alkylphenol containing the para attachment of the alkyl group is from about 75
10 to about 95 weight percent of the total alkylphenol. More preferably, the
11 alkylphenol containing the para attachment of the alkyl group is from about 80
12 to about 95 weight percent of the total alkylphenol.

13
14 In one preferred embodiment, the alkyl group of said alkylphenol contains
15 from 25 to 100 mole percent predominantly straight-chain alkyl groups of from
16 15 to 35 carbon atoms and from 75 to 0 mole percent of the alkyl groups are
17 branched-chain, such as polypropenyl, of from 9 to 18 carbon atoms. More
18 preferably, the alkyl group of said alkylphenol contains from 35 to 100 mole
19 percent predominantly straight-chain alkyl groups of from 15 to 35 carbon
20 atoms and from 65 to 0 mole percent of the alkyl groups are branched-chain,
21 such as polypropenyl, of from 9 to 18 carbon atoms. In yet another preferred
22 embodiment, the alkyl group of said alkylphenol contains from 40 to 70 mole
23 percent predominantly straight-chain alkyl groups of from 15 to 35 carbon
24 atoms and from 60 to 30 mole percent of the alkyl groups are branched-chain,
25 such as polypropenyl, of from 9 to 18 carbon atoms. Most preferably, the
26 alkyl group of said alkylphenol contains approximately 50 mole percent
27 predominantly straight-chain alkyl groups of from 15 to 35 carbon atoms and
28 approximately 50 mole percent of the alkyl groups are branched-chain, such
29 as polypropenyl, of from 9 to 18 carbon atoms.

30
31 The preferred oil-soluble Group II metal overbased natural or synthetic
32 hydrocarbyl sulfonic acid, sulfonate, or mixture thereof useful for the process

1 of the present invention are single-ring alkyl aromatic hydrocarbyl sulfonic
2 acid, sulfonate, or mixture thereof, more preferred are alkylbenzene or
3 alkyltoluene sulfonic acids, sulfonates or mixtures thereof. The alkyl group on
4 the aromatic ring can be from about 6 to about 60 carbon atoms. Preferably,
5 the alkyl group is from about 10 to about 40 carbon atoms and most
6 preferably from about 20 to about 28 carbon atoms.

7
8 The alkyl group of the mono-alkyl or di-alkyl substituted ethylene carbonate
9 useful for carrying out the process of the present invention is preferably a
10 mono-substituted methyl group, i.e., the alkylene carbonate is propylene
11 carbonate. Most preferably, the alkylene carbonate is ethylene carbonate.

12
13 The process of the instant invention is particularly useful for preparing highly
14 overbased sulfurized alkylphenols possessing a Total Base Number of greater
15 than about 240, and preferably from about 250 to about 350, more preferably
16 from about 260 to about 290.

17
18 In the process of the present invention, the Group II metal oxide, hydroxide or
19 C₁-C₆ alkoxide is selected from the group consisting of calcium, barium,
20 magnesium and strontium oxide, hydroxide or C₁-C₆ alkoxide and mixtures
21 thereof. Preferably, the Group II metal oxide, hydroxide or C₁-C₆ alkoxide is
22 Dolomite comprising Ca(OH)₂.Mg(OH)₂. Most preferably, the Group II metal
23 oxide, hydroxide or C₁-C₆ alkoxide is calcium hydroxide.

24
25 As used herein, the term "Group II metal" means calcium, barium,
26 magnesium, and strontium. Preferably, the Group II metal is selected from
27 the group consisting of calcium, magnesium, barium, and mixtures thereof.
28 Most preferably, the Group II metal is calcium.

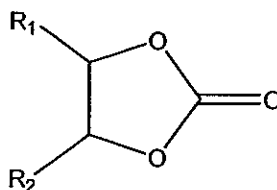
29
30 In the present process, the alkanol contains at least 6 carbon atoms, and
31 typically from about 8 to about 13 carbon atoms. Preferably, the alkanol is
32 isodecyl alcohol.

1 The charge mole ratio of the sulfur to the alkylphenol added in step (b) is
2 about 1.0 to about 1.7, preferably about 1.2 to about 1.6, and more preferably
3 about 1.3 to about 1.5.
4
5 The C₂-C₁₀ alkylene glycol of the present process is preferably ethylene
6 glycol.
7
8 The process of the present invention may be carried out in a batch or a
9 continuous process. It is believed that small changes in pressure will have
10 little effect on the carbonation process of the present invention.
11
12 The present invention is also directed to the novel and unexpected discovery
13 that the Group II metal overbased sulfurized alkylphenol products made when
14 the carbonation step is carried out using ethylene carbonate have superior
15 properties of low color, 3.5 or lower, as measured using ASTM Test
16 No. D 6045, and hydrolytic stability as measured by a modification of ASTM
17 Test No. 2619, as defined below, wherein the TBN of the Group II metal
18 overbased sulfurized alkylphenols decreases less than 10 percent, and
19 preferably less than 8 percent, after the addition of 2.0 percent water and after
20 6 days at 80°C.
21
22 Hydrolytic instability occurs when water is present, but exclusion of water from
23 most systems is impossible. It is also known that overbased sulfurized
24 alkylphenol compositions with high TBN, greater than 250, results in
25 increased hydrolytic instability and increased viscosity. Hydrolytic stability of
26 the Group II metal overbased sulfurized alkylphenols is an extremely
27 important property, particularly in marine crankcase use where water
28 exposure is common. Accordingly, there is a need to develop high TBN
29 Group II metal overbased sulfurized alkylphenol compositions that are
30 hydrolytically stable.

1 Low color is known to be a very desirable characteristic in commercial
2 lubricating oil additives, including detergents and dispersants. It has been
3 discovered that the Group II metal overbased sulfurized alkylphenol
4 compositions of the present invention have low color in comparison with the
5 prior art preparations. Furthermore, we have found that the amount of sulfur
6 added during the sulfurization step for the preparation of the sulfurized
7 alkylphenol in the present process has no discernable effect on its color.

8 The present invention is also directed to a process for the in situ delivery of
9 equimolar quantities of alkylene glycol and carbon dioxide to a reaction
10 mixture, wherein said reaction mixture requires the presence of said alkylene
11 glycol and said carbon dioxide as reactants, said process comprising
12 delivering to said reaction mixture:

13 an alkylene carbonate selected from ethylene carbonate or a mono-alkyl or
14 di-alkyl substituted ethylene carbonate having the following structure:



15
16 wherein R₁ and R₂ are independently hydrogen or alkyl containing one to
17 three carbon atoms; in the presence of water; and under reaction conditions
18 sufficient to hydrolyze the alkylene carbonate to alkylene glycol and carbon
19 dioxide.

20 Preferably, the hydrolysis of the alkylene carbonate to the alkylene glycol and
21 carbon dioxide is carried out at a temperature in the range of about 150°C to
22 about 215°C.

1

BRIEF DESCRIPTION OF THE DRAWINGS

2 Figure 1 shows a comparison of the effect of the addition of water on the
3 hydrolytic stability, represented by the percent TBN retained, of Test
4 Examples 1-4, the products of the present invention, and Comparative
5 Examples D-G. The data used to prepare Figure 1 are also shown in Table III
6 in the Examples section.

7 Figure 2 shows a comparison of color measurements for Test Example 12
8 and Comparative Examples H-L.

9

DETAILED DESCRIPTION OF THE INVENTION

10

DEFINITIONS

11 As used herein, the following terms have the following meanings unless
12 expressly stated to the contrary:

13

14 The term "alkoxide" means a compound which can be formed as the reaction
15 product of an alcohol and a reactive metal.

16

17 The term "alkylene glycol" means an aliphatic diol having two hydroxy groups
18 on adjacent carbon atoms.

19

20 The term "alkylphenol" means a phenol group having one or more alkyl
21 substituents, at least one of which has a sufficient number of carbon atoms to
22 impart oil solubility to the phenol.

23

24 The term "hydrocarbyl sulfonate" means a sulfonate having one or more
25 sulfonate groups having one or more hydrocarbyl substituents.

26

1 The term "hydrolytic stability" means the stability of Group II overbased
2 sulfurized alkylphenols in the presence of water at elevated temperatures.
3 ASTM Test No. 2619 was modified for determining the hydrolytic stability of
4 the Group II overbased sulfurized alkylphenols. The following protocol was
5 followed for all hydrolytic stability determinations:

6

7 Group II overbased sulfurized alkylphenols samples were placed in
8 commercial finished marine oil to obtain a final TBN of 8 for the samples.
9 Water ranging from 0% to 2.0% was added to the samples drop-wise at a rate
10 of 0.5 gram per minute while agitating the samples with a peristaltic pump at a
11 rate of 500 rpm. Agitation of the samples at 500 rpm was continued for an
12 additional 10 minutes after the addition of the water. The samples were
13 covered to prevent loss of water and placed in an oven at 80°C for 6 days. An
14 aliquot of the top layer of the samples containing the oil was carefully
15 removed to determine the TBN using ASTM Test No. D 2896.

16

17 Use of the term "ethylene carbonate" includes alkyl-substituted alkylene
18 carbonate, such as propylene carbonate and the like.

19

20 The term "overbased" means alkaline earth metal alkylphenols in which the
21 ratio of the number of equivalents of an alkaline earth metal to the number of
22 equivalents of the alkylphenol is greater than 1.

23

24 The term "reacting equivalent" means any material equivalent to ethylene
25 glycol and carbon dioxide, such as the carbonic acid half ester.

26

27 The term "sulfurization agent" means a material capable of sulfurizing the
28 alkylphenols of the present invention.

29

30 The term "Total Base Number" or "TBN" refers to the amount of base
31 equivalent to milligrams of KOH in one gram of sample. Thus, higher TBN
32 numbers reflect more alkaline products, and therefore a greater alkalinity

1 reserve. The TBN of a sample can be determined by ASTM Test No. D 2896
2 or any other similar procedure.

3
4 Unless otherwise specified, all percentages are in weight percent and the
5 pressure is atmospheric pressure.

6
7 As noted above, this invention is directed to a novel process for the rapid
8 carbonation of sulfurized alkylphenates using ethylene carbonate or alkylene-
9 substituted ethylene carbonate. We have discovered ethylene carbonate in
10 the carbonation step for the preparation of overbased sulfurized alkylphenates
11 can be used as both a source of carbon dioxide and ethylene glycol. Under
12 the reaction conditions using ethylene carbonate, carbonation time is reduced
13 from 6 hours to less than 1 hour, thus reducing the total preparation time for
14 making overbased sulfurized alkylphenols to nearly one-half the time
15 necessary in the prior art processes.

16
17 The present process overcomes many of the limitations of time and
18 temperature control that are critical in the conventional carbonation process.
19 This new process produces carbon dioxide in a highly reactive form that is
20 also better dispersed.

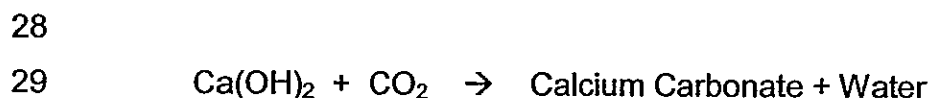
21
22 The presence of glycol is essential for good overbasing. Glycol is not merely
23 a solvent but rather plays an active role in phenate carbonation. The in situ
24 production of glycol in the present process provides timely and sufficient
25 glycol for the carbonation process and overcomes the problems encountered
26 in the prior art processes.

27
28 In the prior art carbonation process, reaction conditions, especially
29 temperature, must be carefully monitored to avoid "starving" the reaction of
30 glycol. In the present process, no similar issue of glycol starvation is
31 observed. Without being bound by any theory, it is believed that this may be
32 true because carbon dioxide and ethylene glycol are chemically bound in the

1 form of a carbonic acid half ester of ethylene glycol, as will be described later.
2 Such an intermediate, if present, means that there is always adequate glycol
3 during carbonation. It has now been discovered that ethylene carbonate may
4 be added over 15 minutes at about 186°C with virtually no loss of carbon
5 dioxide and no adverse effect on crude product sediment, TBN or other critical
6 analytical results.

7 It has now been found that ethylene carbonate can be added extremely
8 rapidly during carbonation with negligible escape of gaseous carbon dioxide
9 from the reaction. Although there is some remaining hydrogen sulfide gas
10 evolution during the carbonation step, there is very little carbon dioxide
11 evolution. In one experiment, we added ethylene carbonate over a 15-minute
12 period starting at about 177°C. Even with such rapid addition, essentially no
13 carbon dioxide evolution occurred as demonstrated by the low crude product
14 sediment (0.8%). It is believed that if the carbon dioxide escapes, then less
15 Ca(OH)_2 is incorporated in the product, thus, resulting in higher sediment.
16 Lack of significant carbon dioxide evolution was also observed as measured
17 by a dry test meter for measuring gas. The explanation for the high carbon
18 dioxide incorporation may involve a mechanism wherein carbon dioxide is not
19 present as such but rather an intermediate half ester of carbonic acid,
20 explained in greater detail below, acts as the carbonation source.

21
22 The prior art carbonation process produces one molar equivalent of water for
23 an equimolar reaction of Ca(OH)_2 with carbon dioxide. In the prior art
24 processes for making overbased sulfurized alkylphenols, the carbonate is
25 incorporated in a complex form and not simply as calcium carbonate.
26 However, for simplicity, we can represent the formation of calcium carbonate
27 from Ca(OH)_2 and carbon dioxide as:

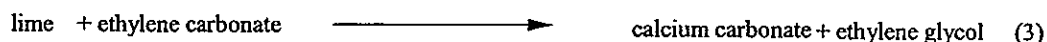
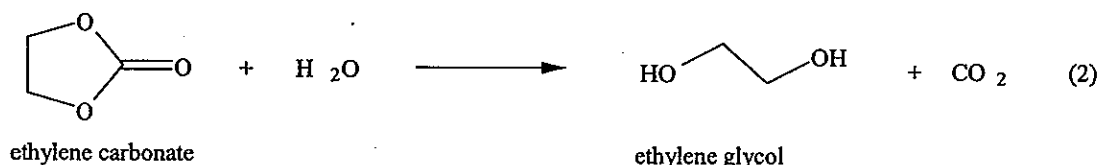
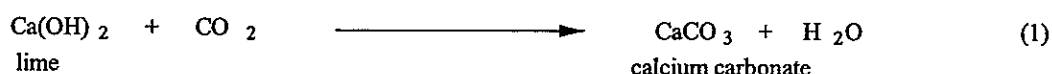


1 By contrast, the present process requires one water molecule to react with the
 2 ethylene carbonate to form carbon dioxide and ethylene glycol (or the
 3 carbonic acid half ester). The net effect is that the present process both
 4 produces and consumes an equal quantity of water, thus eliminating the need
 5 to remove water.

6 The water produced during carbonation is generated at a temperature well
 7 above the boiling point of water. For this reason, the carbonation temperature
 8 must be carefully selected to facilitate water removal, thus driving the reaction
 9 to completion. However, if the temperature is too high, excessive quantities of
 10 glycol will steam distill putting the reaction on a path toward glycol starvation.

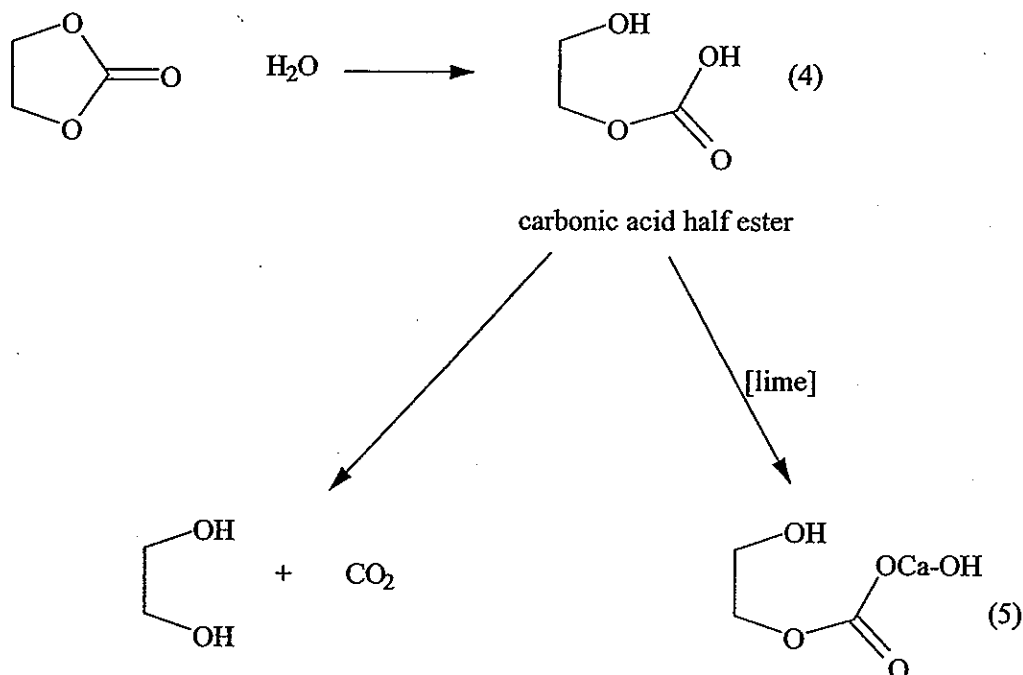
11
 12 In the prior art carbonation process employing ethylene glycol and carbon
 13 dioxide, carbon dioxide reacts with Ca(OH)_2 to form carbonate and water.
 14 Without being bound by any theory, it is believed that when ethylene
 15 carbonate is the source for carbon dioxide and ethylene glycol, no net water is
 16 produced during the formation of the sulfurized alkylphenate carbonate. This
 17 may be explained by equations (1) and (2) below. Thus, the consumption of
 18 Ca(OH)_2 to form carbonate is accompanied by the formation of one molar
 19 equivalent of water. Likewise, the hydrolysis of ethylene carbonate to form
 20 glycol and carbon dioxide consumes one molar equivalent of water. As
 21 shown in equation (3), the overall reaction equation of Ca(OH)_2 reacting with
 22 ethylene carbonate forms calcium carbonate without formation of water.

23



1 Accordingly, the above reactions may explain why water is not formed during
2 the present carbonation process. However, the above equations are a
3 simplification since in the actual process the carbonate is part of an
4 alkylphenate structure rather than a simple salt of calcium. It has now been
5 found that the carbonation of the present process proceeds well even at
6 temperatures up to about 200°C with little or no loss of carbon dioxide.
7 Furthermore, carbonation with ethylene carbonate proceeds at a remarkably
8 fast rate for temperatures in the range of about 162°C to about 200°C. This
9 was not anticipated. The general thinking prior to this invention was that
10 consumption of particulate lime, as well as incorporation of oxidized glycol
11 intermediates, within the alkylphenate structure would rate limit the
12 carbonation process. The very rapid carbonation reaction with ethylene
13 carbonate is notably different and produces nearly the same level of carbon
14 dioxide incorporation under varying conditions of temperature and ethylene
15 carbonate addition rate.
16
17 Without being bound by any theory, it is predicted that the reaction of ethylene
18 carbonate with water may proceed by either of two paths as shown below.
19 The first step is the hydrolytic cleavage of the cyclic carbonate ring
20 (accelerated by base catalysis) to form a half ester of carbonic acid (4).
21 Intermediate (4) may subsequently react with lime to form the calcium salt (5)
22 or may fragment further to form carbon dioxide and ethylene glycol. For
23 temperatures below about 200°C, formation of intermediate (5) is probably
24 favored over free carbon dioxide and ethylene glycol. When the ethylene
25 carbonate addition temperature is increased in excess of about 200°C, there
26 is a reduction in the phenate carbonate level, which we attribute to the
27 formation of free carbon dioxide and its subsequent partial loss through the
28 reaction vent.
29

- 1 This mechanistic interpretation is logical in terms of an expected rapid
- 2 neutralization of intermediate (4) with $\text{Ca}(\text{OH})_2$ and is further supported by the
- 3 observation of rapid and complete phenate carbonation which is essentially
- 4 insensitive to the reaction conditions of time and temperature.

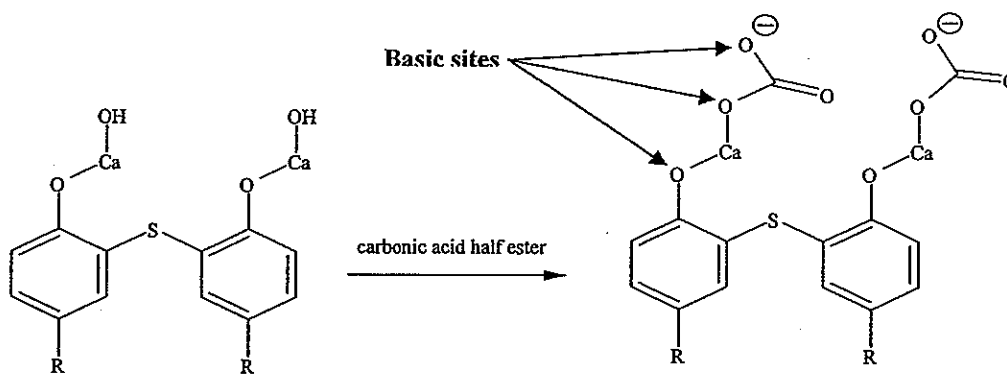


- 5
- 6 Thus, calcium salt (5) is the chemical species that may be responsible for
- 7 delivering incipient carbon dioxide and ethylene glycol to the sulfurized
- 8 phenate intermediate. Intermediate (5) may also explain why ethylene glycol
- 9 is not readily lost from the reaction mixture even at about 200°C . Traditional
- 10 sulfurized phenate carbonation is limited by conditions of reaction temperature
- 11 owing to steam distillation of ethylene glycol from the reaction medium. Under
- 12 conditions of ethylene glycol "starvation", sulfurized phenate reactions are
- 13 known to give low carbon dioxide incorporation and an increase in the crude
- 14 product sediment.
- 15
- 16 The percentage of carbon dioxide incorporation relative to a value calculated
- 17 assuming quantitative hydrolysis of ethylene carbonate to carbon dioxide and
- 18 ethylene glycol may be determined for the process of the present invention.

1 This value remains fairly constant in a range of 92% to 96%. This high
2 efficiency for carbonate formation is likely a result of the efficiency of ethylene
3 carbonate hydrolysis rather than the efficiency in carbon dioxide trapping,
4 which also explains why very rapid ethylene carbonate addition rates do not
5 significantly alter the percentage of carbon dioxide formation.

6
7 A simplified molecular structure for an overbased sulfurized carbonate
8 alkylphenate is shown below. For this structure, there would be three basic
9 sites per mole of alkylphenol as shown. From reaction stoichiometry and
10 product analytical data for various overbased sulfurized alkylphenate
11 samples, it has been found that, on average, they contain 3.4 basic sites per
12 mole of alkylphenol. Additional basic sites, not shown in the simplified
13 overbased sulfurized carbonate alkylphenate, include the glycol residues
14 (oxylates, glycolates, etc.) that form an integral part of the phenate structure.

Ethylene Carbonate Carbonation



28 The rate of addition of ethylene carbonate has been tested over a range of
29 addition times (15 to 120 minutes) and temperature (162°C-200°C). The
30 incorporation of carbonate and crude product sediment are relatively immune
31 to these differences in reaction conditions. The addition of ethylene
32 carbonate is relatively exothermic and this can be seen when the ethylene
33 carbonate is added very rapidly (for example, in less than 20 minutes). Under
34 such conditions, that reaction temperature will rise rapidly from about 162°C

1 (the start of ethylene carbonate addition). At approximately 186°C, some
2 excess foaming was observed. However, even under these conditions, the
3 incorporation of carbonate is very high. On the other hand, ethylene
4 carbonate addition at temperatures in excess of 210°C should be avoided
5 since an increase in reaction gas evolution and some reduction in the level of
6 product carbonate was observed at these high temperatures. At
7 temperatures above about 200°C, the breakdown of the carbonic acid half
8 ester (1) to carbon dioxide and ethylene glycol appears to be reaction rate
9 competitive with neutralization of the acid to the calcium salt (2).

10

11 The reduction in the time for the preparation of overbased sulfurized
12 alkylphenates results in doubling the capacity for production of the overbased
13 sulfurized alkylphenates, without any loss in the quality of the product by
14 infrared spectral analysis. The chemical and physical properties of the
15 product of the present process are also good, including high base content, low
16 crude product sediment and fast filtration rates.

17 Most surprising was the discovery that the product of the present invention
18 has increased hydrolytic stability and low color. Both hydrolytic stability and
19 low color are extremely desirable and important characteristics for commercial
20 Group II overbased sulfurized alkyl phenol compositions. The product of the
21 present invention has increased hydrolytic stability, as measured by a
22 modification of ASTM Test No. D 2619, as defined above, compared to the
23 prior art product even after 6 days at 80°C after the addition of water. Lower
24 color, as measured by ASTM Test No. D 6045, is also observed in the
25 Group II overbased sulfurized alkyl phenol compositions of the present
26 invention as compared to those prepared by the prior art processes.

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1 After the addition of ethylene glycol, the temperature was increased from
2 149°C to 177°C over the next hour.
3
4 270.9 grams of ethylene carbonate was added to the reaction mixture over
5 2 hours. After the addition of ethylene carbonate, the temperature was
6 increased from 177°C to 210°C over the next 30 minutes and the vacuum was
7 increased from 730 mm Hg to 30 mm Hg over the next 15 to 20 minutes.

8 The reaction mixture was then held at 210°C and 30 mm Hg for 30 minutes
9 after which the vacuum was broken with nitrogen gas.

10

11 The product was collected after filtration. The product had a TBN of 259 and
12 crude product sediment of 1.6%.

13

14 The results of Test Examples 2-6 and Comparative Examples B and C
15 depicted in Table II illustrate the effects of varying certain parameters and
16 reaction conditions when ethylene carbonate is used in the carbonation step.

17

18

Test Example 2

19

Effect of reduction of ethylene glycol on preparation
of overbased sulfurized alkylphenols

20

21

22 The procedure set forth above in Test Example 1 was followed, except the
23 amount of ethylene glycol was reduced by 50 weight percent, that is,
24 244.5 grams was added to the reaction mixture. The results in Table II show
25 that reduction in ethylene glycol is compensated for by the production of
26 ethylene glycol from the hydrolysis of ethylene carbonate, thus there was no
27 appreciable increase in the crude product sediment, 1.9%. A TBN of 255 was
28 obtained for the product.

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1 Comparative Example B

2 Effect of isodecyl alcohol on preparation of overbased sulfurized
3 alkylphenols when carbonation is carried out using ethylene carbonate

4
5 The procedure set forth above in Test Example 1 was followed, except the
6 amount of isodecyl alcohol was reduced by 50%, that is, 243.4 grams was
7 added to the reaction mixture. The results in Table II show that the isodecyl
8 alcohol plays a role in the preparation of the overbased sulfurized
9 alkylphenates beyond simply reducing the viscosity of the uncarbonated
10 product. Reduction of isodecyl alcohol may cause high crude product
11 sediment levels, 42%, which is probably a result of poor dehydration and
12 sulfurization. The TBN was also lower, 243.

13
14 Comparative Example C

15 Effect of ethylene glycol on preparation of overbased sulfurized
16 alkylphenols when carbonation is carried out using ethylene carbonate

17
18 The procedure set forth above in Test Example 1 was followed, except that
19 ethylene glycol was eliminated from the dehydration and sulfurization step in
20 the preparation of the overbased sulfurized alkylphenates. The only ethylene
21 glycol available in the reaction mixture was from the hydrolysis of ethylene
22 carbonate added in the carbonation step. The results show that ethylene
23 glycol is required for the dehydration and sulfurization step prior to the
24 carbonation step. The crude product sediment was 24% and the TBN
25 obtained was 66.4.

26
27 The experimental conditions used in Test Examples 1-7 and the Comparative
28 Examples A-C are summarized below in Table I.

Table I

Ex	Amount of Reaction Components Charge Mole Ratio relative to the Alkylphenol						Addition of EC ¹ Time in Minutes
	Alkylphenol	Isodecyl Alcohol	Ethylene Glycol	Calcium Hydroxide	Ethylene Carbonate	Hydrocarbyl Sulfonate	
1	1.000	1.000	1.300	1.766	1.000	1.000	120
2	1.000	1.000	0.650	1.766	1.000	1.000	120
3	1.000	1.000	0.650	1.766	0.900	1.000	60
4	1.000	0.745	0.650	1.766	0.900	1.000	60
5	1.000	0.909	0.423	1.766	0.900	1.000	60
6	1.000	0.909	0.423	1.766	0.900	1.000	30
7	1.000	1.000	0.650	1.766	0.900	1.000	15
A	1.000	1.034	1.310	1.766	CO ₂ * 0.893	1.000	NA ²
B	1.000	0.500	1.300	1.766	1.000	1.000	120
C	1.000	0.909	0.0	1.766	1.000	1.000	60

¹ Ethylene carbonate.

* Carbon dioxide replaced the carbon dioxide obtained from the hydrolysis of ethylene carbonate in the Test Examples.

² No ethylene carbonate added.

The results obtained in the above Test Examples 1-7 and the Comparative Examples A-C are given below in Table II.

Table II

Ex	Final Product Weight in grams	Weight Percent of Final Product				TBN
		Sulfur	Calcium	CO ₂	Sediment	
1	2253	4.1	9.5	5.5	1.6	259
2	2083	3.5	9.5	5.6	1.9	255
3	2023	3.5	9.9	5.3	0.8	265
4	2040	3.7	9.6	5.1	1.0	260
5	1996	3.5	9.7	5.3	1.0	263
6	2041	3.5	9.1	5.0	4.8	250
7	2024	3.5	9.7	5.3	0.8	263
A	1769	3.5	9.2	5.2	1.2	249
B	2291	3.6	9.0	4.9	42	243
C	1904	2.8	2.4	0.3	24	66

1
2 Hydrolytic stability studies
3

4 The Group II metal overbased sulfurized alkylphenol products of this invention
5 has increased hydrolytic stability compared to the Group II metal overbased
6 sulfurized alkylphenols prepared using the conventional carbonation process
7 employing ethylene glycol and carbon dioxide.
8

9 The hydrolytic stability of the Group II overbased sulfurized alkyl phenol
10 compositions of the present invention was determined using a modification of
11 ASTM Test No. D 2619. The modified test, as defined above, measures the
12 hydrolytic stability of a product by measuring its TBN loss upon exposure to
13 moisture. Greater TBN loss reflects poorer hydrolytic stability.
14

15 Hydrolytic stability data were collected in experiments where water was added
16 to the overbased sulfurized alkylphenol samples and the retention of TBN was
17 measured. The data given in Table III below and in Figure 1 show that the
18 overbased sulfurized alkylphenols prepared by the process of the present
19 invention are more hydrolytically stable than those prepared using the
20 conventional carbonation process as demonstrated by the percent of TBN
21 retention.
22

23 Comparative Examples D-G were prepared using the procedure of
24 Comparative Example A above. Test Examples 8-11 were prepared using the
25 procedure of Test Example 1 above. Tests were conducted with and without
26 the addition of water. The results of the tests are given in Table III and in
27 Figure 1.
28

Table III

HYDROLYTIC STABILITY			
Examples	Amount of Water Added to Blend	TBN of Sample after 6 Days at 80°C	Percent TBN Retention
D	0.0 wt.%	7.4846	100
E	0.5 wt.%	6.4115	85.66
F	1.0 wt.%	6.2482	83.48
G	2.0 wt.%	6.1505	82.18
8	0.0 wt.%	6.8373	100
9	0.5 wt.%	6.6935	97.9
10	1.0 wt.%	6.6432	97.16
11	2.0 wt.%	6.4792	94.76

The results of the hydrolytic stability studies clearly show that the Group II overbased sulfurized alkylphenols prepared by the process of the present invention have consistently better TBN retention than that observed for the Group II overbased sulfurized alkylphenols of Comparative Examples D-G.

Color studies

Color studies were conducted to determine the degree of color of the Group II overbased sulfurized alkylphenols prepared by the process of the present invention as compared to that of the Group II overbased sulfurized alkylphenols prepared using ethylene glycol and carbon dioxide.

Test Examples 12-19 were prepared using the procedure of Test Example 1. Comparative Examples H-L were commercial Group II sulfurized alkylphenols prepared from C₁₀-C₁₅ alkylphenol using ethylene glycol and carbon dioxide.

Color was determined using ASTM Test No. D 6045. The results obtained using a Lovibond PFX995 Tintometer are given in Table IV and Figure 2.

The results show that the Group II metal overbased sulfurized alkylphenol products prepared by the process of this invention, Test Example 12, have less color than observed for the commercial Group II metal overbased sulfurized alkylphenols, Comparative Examples H-L.

The effect of sulfur concentration on the amount of color was also determined using ASTM Test No. D 6045. The experimental results given in Table IV below show that under the standard experimental conditions (see Test Example 1 above), reduction in sulfur during the sulfurization step of the present process does not reduce the color of the overbased sulfurized alkylphenol products prepared by the process of the present invention, Test Examples 13-19.

Table IV

Example	Sulfur CMR*	TBN	COLOR			
			Sample 1	Sample 2	Sample 3	Average
12	1.36	259	2.5	2.5	2.5	2.5
13	1.29	259	3.4	3.5	3.5	3.5
14	1.25	258	3.0	3.0	3.0	3.0
15	1.21	265	3.3	3.3	3.3	3.3
16	1.18	262	3.0	3.0	3.0	3.0
17	1.10	269	3.4	3.5	3.5	3.5
18	0.99	267	3.0	3.2	3.2	3.2
19**	0.90	252	---	---	---	Hazy, not bright
H	100	250	6.5	6.9	6.8	6.7
I	100	250	5.5	5.5	5.6	5.5
J	100	250	3.8	3.8	3.8	3.8
K	100	250	4.6	4.6	4.7	4.6
L	100	250	4.6	4.6	4.6	4.6

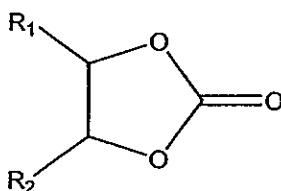
* CMR is charge mole ratio of sulfur to the alkylphenol.

** Color of Test Example 19 could not be determined.

1 WHAT IS CLAIMED IS:

2
3 1. A process for preparing Group II metal overbased sulfurized
4 alkylphenols which comprises:

5 forming a reaction mixture by combining a sulfurized alkylphenol wherein
6 the alkyl group contains a sufficient number of carbon atoms to render
7 oil-soluble the resulting Group II metal overbased sulfurized alkylphenol,
8 an alkanol containing about 6 to about 15 carbon atoms, a Group II
9 metal oxide, hydroxide or C₁-C₆ alkoxide, a C₂-C₁₀ alkylene glycol and
10 with an alkylene carbonate selected from ethylene carbonate or a
11 mono-alkyl or di-alkyl substituted ethylene carbonate, said alkylene
12 carbonate having the following structure:



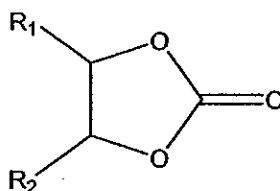
14 wherein R₁ and R₂ are independently hydrogen or alkyl containing one to
15 three carbon atoms; and wherein the contacting is carried out for a time
16 and at a temperature sufficient to form in situ carbon dioxide and
17 alkylene glycol, or a reacting equivalent, to form a product comprising a
18 Group II earth metal overbased sulfurized alkylphenol.

19 2. A process for preparing Group II metal overbased sulfurized
20 alkylphenols which comprises the steps of:

21 (a) forming a reaction mixture by combining a sulfurized alkylphenol
22 wherein the alkyl group contains a sufficient number of carbon
23 atoms to render oil-soluble the resulting Group II metal overbased
24 sulfurized alkylphenol, an alkanol containing about 6 to about

15 carbon atoms, a Group II metal oxide, hydroxide or C₁-C₆ alkoxide, and a C₂-C₁₀ alkylene glycol; and

- (b) contacting said reaction mixture with an alkylene carbonate selected from ethylene carbonate or a mono-alkyl or di-alkyl substituted ethylene carbonate, said alkylene carbonate having the following structure:

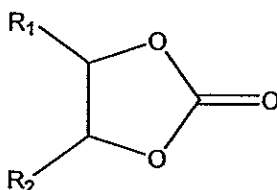


wherein R₁ and R₂ are independently hydrogen or alkyl containing one to three carbon atoms; and wherein the contacting is carried out for a time and at a temperature sufficient to form in situ carbon dioxide and alkylene glycol, or a reacting equivalent, to form a product comprising a Group II earth metal overbased sulfurized alkylphenol.

3. A process for preparing Group II metal overbased sulfurized alkylphenols which comprises the steps of:

- (a) forming a first reaction mixture by combining an alkylphenol wherein the alkyl group contains a sufficient number of carbon atoms to render oil-soluble the resulting Group II metal overbased sulfurized alkylphenol, an oil-soluble Group II metal overbased natural or synthetic hydrocarbyl sulfonic acid, sulfonate, or mixtures thereof, and an alkanol containing about 6 to about 15 carbon atoms, the temperature of said first reaction mixture being at least about 40°C;

- 1 (b) contacting said first reaction mixture with a second reaction mixture
2 comprising a Group II metal oxide, hydroxide or C₁-C₆ alkoxide; a
3 sulfurization agent and an inert hydrocarbon diluent at a
4 temperature and for a time sufficient to effect sulfurization of the
5 alkylphenol to form a third reaction mixture;
- 6 (c) contacting said third reaction mixture with C₂-C₁₀ alkylene glycol to
7 form a fourth reaction mixture; and
- 8 (d) contacting said fourth reaction mixture with an alkylene carbonate
9 selected from ethylene carbonate or a mono-alkyl or di-alkyl
10 substituted ethylene carbonate, said alkylene carbonate having the
11 following structure:



12

13 wherein R₁ and R₂ are independently hydrogen or alkyl containing
14 one to three carbon atoms; and wherein said contacting is carried
15 out for a time and at a temperature sufficient to form in situ carbon
16 dioxide and alkylene glycol, or a reacting equivalent, to form a
17 product comprising a Group II earth metal overbased sulfurized
18 alkylphenol.

- 19 4. The process of any one of claims 1-3 wherein the sulfurized alkylphenol
20 is a Group II metal sulfurized alkylphenate.
- 21 5. The process of any one of claims 1 or 2 further comprising an oil-soluble
22 Group II metal overbased natural or synthetic hydrocarbyl sulfonic acid,
23 sulfonate, or mixtures thereof.

- 1 6. The process of any one of claims 1-3 wherein the alkylene carbonate is
2 added to the reaction mixture over a time period of about 5 minutes to
3 about 120 minutes.
- 4 7. The process of claim 6 wherein the alkylene carbonate is added to the
5 reaction mixture over a time period of about 15 minutes to about
6 90 minutes.
- 7 8. The process of claim 7 wherein the alkylene carbonate is added to the
8 reaction mixture over a time period of about 30 minutes to about
9 60 minutes.
- 10 9. The process of any one of claims 1-3 wherein the temperature is
11 maintained below about 215°C.
- 12 10. The process of claim 9 wherein the temperature is maintained between
13 150°C and 210°C.
- 14 11. The process of any one of claims 1-3 wherein the alkyl group of the
15 alkylene carbonate is a methyl group.
- 16 12. The process of any one of claims 1-3 wherein the alkylene carbonate is
17 ethylene carbonate.
- 18 13. The process of any one of claims 1-3 wherein the ratio of the alkylene
19 carbonate to the alkylphenol is 0.6 to 1.5 weight percent.
- 20 14. The process of claim 3 wherein the charge mole ratio of the sulfur to the
21 alkylphenol is about 1.0 to about 1.7.
- 22 15. The process of claim 14 wherein the charge mole ratio of the sulfur to
23 the alkylphenol is about 1.3 to about 1.5.

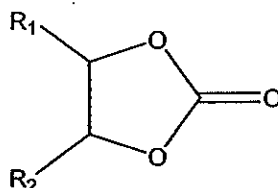
- 1 16. The process of claim 3 wherein in step (c), after contacting the third
2 reaction mixture with a C₂-C₁₀ alkylene glycol, the temperature of the
3 system is raised, if necessary, from that of step (b) to between about
4 120°C and about 190°C.
- 5 17. The process of claim 3 wherein in step (c) the C₂-C₁₀ alkylene glycol
6 addition is conducted at from about 100°C to about 190°C.
- 7 18. The process of claim 17 wherein in step (c) the C₂-C₁₀ alkylene glycol
8 addition is conducted at from 125°C to 165°C.
- 9 19. The process of claim 3 further comprising:
- 10 (e) heating the fourth reaction mixture of step (d) under reduced
11 pressure to remove a portion of unreacted C₂-C₁₀ alkylene glycol
12 and carbon dioxide.
- 13 20. The process of claim 19 wherein step (e) is preferably conducted at from
14 about 175°C to about 210°C.
- 15 21. The process of claim 3 further comprising in step (a) or in step (b), or in
16 both steps (a) and (b), the presence of a sulfurization catalyst, wherein
17 the sulfurization catalyst is a hydrogen halide, an ammonium halide, a
18 metal halide or 2-mercaptobenzothiozole.
- 19 22. The process of claim 21 wherein the sulfurization catalyst is a metal
20 halide.
- 21 23. The process of claim 22 wherein the sulfurization catalyst is calcium
22 chloride.
- 23 24. The process of any one of claims 1-3 wherein the alkyl group of the
24 alkylphenol contains from about 25 to about 100 mole percent

- 1 predominantly straight-chain alkyl groups containing from about 15 to
2 about 35 carbon atoms and from about 75 to about 0 mole percent
3 branched-chain alkyl groups containing from about 9 to about 18 carbon
4 atoms.
- 5 25. The process of claim 24 wherein the alkyl group of the alkylphenol
6 contains from about 35 to about 100 mole percent predominantly
7 straight-chain alkyl groups containing from about 15 to about 35 carbon
8 atoms and from about 65 to about 0 mole percent branched-chain alkyl
9 groups containing from about 9 to about 18 carbon atoms.
- 10 26. The process of claim 25 wherein the alkyl group of the alkylphenol
11 contains from about 40 to about 70 mole percent predominantly
12 straight-chain alkyl groups containing from about 15 to about 35 carbon
13 atoms and from about 60 to about 30 mole percent branched-chain alkyl
14 groups containing from about 9 to about 18 carbon atoms.
- 15 27. The process of claim 26 wherein the alkyl group of the alkylphenol
16 contains approximately 50 mole percent predominantly straight-chain
17 alkyl groups containing from about 15 to about 35 carbon atoms and
18 approximately 50 mole percent branched-chain alkyl groups containing
19 from about 9 to about 18 carbon atoms.
- 20 28. The process of any one of claims 1-3 wherein the alkyl group of the
21 alkylphenol is attached predominantly at the para position of the phenol
22 ring.
- 23 29. The process of claim 28 wherein the alkylphenol containing the para
24 attachment of the alkyl group is from about 70 to about 95 weight
25 percent of the total alkylphenol.

- 1 30. The process of claim 29 wherein the alkylphenol containing the para
2 attachment of the alkyl group is from about 80 to about 95 weight
3 percent of the total alkylphenol.
- 4 31. The process of any one of claims 1-3 wherein the alkanol contains about
5 8 to about 13 carbon atoms and the C₂-C₁₀ alkylene glycol is ethylene
6 glycol.
- 7 32. The process of claim 31 wherein the alkanol is isodecyl alcohol.
- 8 33. The process of any one of claims 3 or 5 wherein the hydrocarbyl group
9 of the oil-soluble Group II metal overbased natural or synthetic
10 hydrocarbyl sulfonic acid, sulfonate, or mixtures thereof, is an alkyl
11 aromatic group.
- 12 34. The process of claim 33 wherein the alkyl group of the alkyl aromatic
13 group contains from about 6 carbon atoms to about 60 carbon atoms.
- 14 35. The process of claim 34 wherein the alkyl group of the alkyl aromatic
15 group contains from about 10 carbon atoms to about 40 carbon atoms.
- 16 36. The process of claim 35 wherein the alkyl group of the alkyl aromatic
17 group contains from about 20 carbon atoms to about 28 carbon atoms.
- 18 37. The process of any one of claims 1-3 wherein the Group II metal oxide,
19 hydroxide or C₁-C₆ alkoxide is selected from the group consisting of
20 calcium, barium, and magnesium oxide, hydroxide or C₁-C₆ alkoxide and
21 mixtures thereof.
- 22 38. The process of claim 37 wherein the Group II metal oxide, hydroxide or
23 C₁-C₆ alkoxide is calcium hydroxide.

- 1 39. The process of claim 37 wherein the Group II metal oxide, hydroxide or
2 C₁-C₆ alkoxide is Dolomite comprising Ca(OH)₂.Mg(OH)₂.
- 3 40. A product made by the process of any one of claims 1-3.
- 4 41. A product made by the process of claim 19.
- 5 42. A product made by the process of claim 21.
- 6 43. A detergent-dispersant additive comprising Group II metal overbased
7 sulfurized alkylphenols, said additive being characterized by the
8 following properties:
- 9 (a) a color of 3.5 or lower, as measured using ASTM Test No. D 6045;
10 and
- 11 (b) an increased hydrolytic stability as measured by a modified ASTM
12 Test No. 2619 wherein the TBN of the Group II metal overbased
13 sulfurized alkylphenols decreases less than 10 percent after
14 dilution of the material in finished marine oil to a TBN of 10 and the
15 addition of 2.0 percent water and after 6 days at 80°C.
- 16 44. The detergent-dispersant additive of claim 43 wherein the TBN of the
17 Group II metal overbased sulfurized alkylphenols decreases less than
18 8 percent after dilution of the material in finished marine oil to a TBN of 8
19 and the addition of 2.0 percent water and after 6 days at 80°C.
- 20 45. A process for the in situ delivery of equimolar quantities of alkylene
21 glycol and carbon dioxide to a reaction mixture, wherein said reaction
22 mixture requires the presence of said alkylene glycol and said carbon
23 dioxide as reactants, said process comprising delivering to said reaction
24 mixture:

1 an alkylene carbonate selected from ethylene carbonate or a mono-alkyl
2 or di-alkyl substituted ethylene carbonate having the following structure:



3
4 wherein R₁ and R₂ are independently hydrogen or alkyl containing one to
5 three carbon atoms; in the presence of water; and under reaction
6 conditions sufficient to hydrolyze the alkylene carbonate to alkylene
7 glycol and carbon dioxide.

8 46. The process of claim 45 wherein the hydrolysis of the alkylene
9 carbonate to alkylene glycol and carbon dioxide is carried out at
10 temperatures in the range of about 150°C to about 215°C.

11 47. The process of claim 45 wherein the alkyl group of the said alkylene
12 carbonate is a methyl group.

13 48. The process of claim 45 wherein the said alkylene carbonate is ethylene
14 carbonate.