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01 OVERBASED ALKYLATED ALKYL SALICYLATES

02

03 BACKGROUND OF THE INVENTION

04

05 Field of the Invention

06 This invention is directed to overbased alkylated alkyl
07 salicylates which overbased products are suitable for use in
08 lubricating oil compositions used in internal combustion
09 engines. In particular, these additives impart water
10 tolerance, thermal stability, detergency, compatibility and
11 good oxidation performance in such lubricating oil
12 compositions.

13

14 State of the Art

15 Overbased alkylated salicylates are a class of lubricating
16 oil detergents known to impart improved performance
17 (detergency, water tolerance, thermal stability,
18 antioxidancy) to lubricating oil compositions used for
19 lubrication of internal combustion engines.

20

21 Overbased salicylates are prepared by overbasing the
22 corresponding alkylated salicylic acids which, in turn, are
23 typically prepared by first alkylating phenol to form
24 alkylphenol followed by carboxylation via the Kolbe-Schmitt
25 reaction to provide for alkylated salicylic acid. The alkyl
26 group is typically a long chain alkyl group of greater than
27 about 14 carbon atoms so as to impart oil solubility.

28

29 One problem encountered with this synthetic scheme when a
30 substantially linear alkylation feed is employed is that not
31 all of the long chain alkylphenol is readily carboxylated
32 via the Kolbe-Schmitt reaction. Specifically, conventional
33 alkylation of phenol with a substantially linear alkylation
34 feed provides for approximately a 50:50 mixture of ortho-



01 alkylphenol and para-alkylphenol. While the Kolbe-Schmitt
02 reaction readily carboxylates the resulting long chain para-
03 alkylphenol, the resulting long chain ortho-alkylphenol is
04 less reactive and only about 70 percent of total amount of
05 the alkylphenol derived from a substantially linear
06 alkylation feed is typically converted to alkylated
07 salicylic acid during this reaction.

08

09 One method of circumventing this problem is to alkylate an
10 alkyl salicylate (e.g., methyl salicylate) and then subject
11 the resulting alkylated alkyl salicylate to hydrolysis so as
12 to provide for the alkylated salicylic acid. Methods of
13 alkylating alkyl salicylates are disclosed in U.S. Patent
14 Application Serial No. 08/_____ filed concurrently
15 herewith as Attorney Docket No. 005950-367 and entitled
16 "ALKYLATION OF ALKYL SALICYLATE USING A LONG CHAIN CARBON
17 FEED" which application is incorporated herein by reference
18 in its entirety.

19

20 This latter synthetic scheme involves formation of an alkyl
21 salicylate, alkylation of the alkyl salicylate to form an
22 alkylated alkyl salicylate, followed by hydrolysis to form
23 the alkylated salicylic acid. Hydrolysis of the alkylated
24 alkyl salicylate to form alkylated salicylic acid was
25 perceived necessary to later formation of overbased products
26 since the carboxyl (-COOH) group was deemed to be an
27 essential component during overbasing. Specifically,
28 overbased products are prepared by the addition of excess
29 basic metal (i.e., greater than that required to neutralize
30 all of the acidic species on the salicylic acid) optionally
31 using carbon dioxide and it was considered that the carboxyl
32 group played an essential role in the ability of the
33 alkylated salicylic acid to incorporate excess basic metal
34 and carbon dioxide presumably via chelation.

This Sheet Has Been Replaced



01 This invention is directed, in part, to the discovery that
02 alkylated alkyl salicylates can be overbased without
03 hydrolysis of the ester functionality to provide for
04 overbased lubricating oil additives suitable for use in
05 lubricating oil compositions. This discovery is
06 particularly surprising in view of the fact that the
07 overbased products of this invention lack carboxyl (-COOH)
08 functionality but, rather, possess an ester (-COOR)
09 functionality (R being alkyl of from 1 to 6 carbon atoms).
10

11 SUMMARY OF THE INVENTION
12

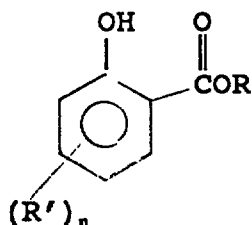
13 This invention is directed, in part, on the discovery that
14 alkylated alkyl salicylates can be directly overbased
15 without hydrolysis of the ester and such overbased products
16 provide for a new class of lubricating oil additives, which
17 exhibit detergency, a source of alkaline reserve, etc. in
18 the finished lubricating oil composition.
19

20 Accordingly, in one of its composition aspects, this
21 invention is directed to a lubricating oil soluble,
22 overbased alkylated alkyl salicylate additive composition
23 having a TBN of from greater than 0 to about 300.
24

25 In another of its composition aspects, this invention is
26 directed to a lubricating oil soluble, overbased alkylated
27 alkyl salicylate composition which is prepared by the
28 process which comprises:
29

30 (a) combining into a diluent from about 15 to about
31 50 weight percent of an alkylated alkyl salicylate
32 based on the total weight of the alkylated alkyl
33 salicylate/diluent composition wherein said
34 alkylated alkyl salicylate is of the formula





08 where R is alkyl of from 1 to about 6 carbon atoms; R'
09 is an alkyl group of from about 15 to about 50 carbon
atom; and n is an integer from 1 to 2:

10 (b) combining a sufficient amount of an alkaline
11 earth metal base into the composition produced in
12 (a) above under conditions wherein the amount of
13 alkaline earth metal is incorporated into the
14 salicylate in excess of that necessary to
neutralize the alkylated alkyl salicylate; and

15 (c) optionally contacting from about 0.1 to about
16 1.5 molar equivalents of carbon dioxide based on
17 each molar equivalent of alkylated alkyl salicylic
18 acid under conditions wherein carbon dioxide is
incorporated into the composition

19 wherein the overbased composition has a TBN of
20 from greater than 0 to about 300.

21 In still another of its composition aspects, this invention
22 is directed to a lubricating oil composition comprising an
23 oil of lubricating viscosity and from about 2 to about 30
24 weight percent of an overbased alkylated alkyl salicylate
25 additive composition having a TBN of from greater than 0 to
26 about 300.

27
28
29 DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS
30

31 This invention is directed to novel overbased alkylated
32 alkyl salicylate compositions which are useful additives for
33 lubricating oil compositions. However, prior to discussing
34



01 this invention in detail, the following terms will first be
02 defined:

03

04 Definitions

05

06 As used herein, the term "Total Base Number" or "TBN" refers
07 to the amount of base equivalent to milligrams of KOH in 1
08 gram of additive. Thus, higher TBN numbers reflect more
09 alkaline products and therefore a greater alkalinity
10 reserve. The Total Base Number for an additive composition
11 is readily determined by ASTM test method number D2896 or
12 other equivalent methods.

13

14 The term "alkaline earth metal" or "Group II metal" means
15 calcium, barium, magnesium, and strontium. Preferably, the
16 Group II metal is selected from the group consisting of
17 calcium, magnesium, barium, and mixtures thereof. Most
18 preferably, the Group II metal is calcium.

19

20 The term "alkaline earth metal base" refers to basic
21 alkaline earth metal materials suitable for use in preparing
22 overbased alkylated alkyl salicylates and, include by way of
23 example, alkaline earth metal oxides, hydroxides and C₁ to C₆
24 alkoxides.

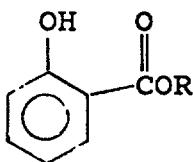
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26 The term "alkyl salicylates" refers to compounds of the
27 formula:

28

29

30



31

32

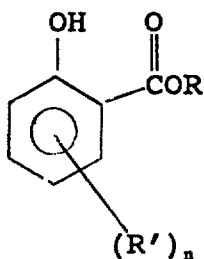
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34

wherein R is an alkyl group of from 1 to 6 carbon
atoms. Preferably, R is an alkyl group of from 1 to 3
carbon atoms and most preferably R is methyl.



The term "alkylated alkyl salicylate" refers to alkyl salicylates which have been alkylated with a long chain carbon feed which alkylated products can be represented by the formula:



where R is as defined above; R' is an alkyl group of from about 15 to 50 carbon atoms; and n is an integer of from 1 to 2 and is preferably 1. In a preferred embodiment, the amount of dialkylation in the product is maintained to about 5% or less.

The term "overbased alkylated alkyl salicylate compositions" refers to compositions prepared by reacting an alkylated alkyl salicylate with an amount of alkaline earth metal base in excess of that necessary to neutralize the acidic species on the alkylated alkyl salicylate and optionally with carbon dioxide. Such overbased products are characterized as having a TBN of greater than 0 and preferably no more than about 300.

The overbased alkylated alkyl salicylate compositions described herein can contain diluent and the term "overbased alkylated alkyl salicylate compositions" is meant to include compositions containing such diluent. Typically, such compositions are manufactured to contain some diluent and, after manufacture, the diluent can be removed, replaced or additional amounts of diluent can be added to provide for an additive composition preferably having from 0 to about 40 weight percent diluent. As such, these additive compositions contain concentrated amounts of the overbased

01 alkylated alkyl salicylate of which only a small amount is
02 added together with other additives to a lubricating oil so
03 as to provide for a fully formulated lubricant composition
04 suitable for use in an internal combustion engine.

05

06 The term "substantially straight-chain alkyl group" means an
07 alkyl group which is attached to the benzene ring of the
08 alkyl salicylate through a secondary, tertiary or quaternary
09 carbon atom and which contains minimal branching in the
10 remainder of the carbon atoms of the alkyl group (i.e., less
11 than 20% of the remaining carbon atoms are tertiary and/or
12 quaternary carbon atoms in the molecular structure of the
13 alkyl group). Suitable substantially straight-chain alkyl
14 groups include, for example, 1-hexadecyl $-\text{[CH}_2(\text{CH}_2)_{14}\text{CH}_3]$ (0%
15 of the carbon atoms are tertiary or quaternary carbon
16 atoms), 4-methyl-1-hexadecyl $-\text{[CH}_2(\text{CH}_2)_2\text{CHCH}_3(\text{CH}_2)_{11}\text{CH}_3]$ (<7% of
17 the carbons are branched), etc.

18

19 Preferably, the substantially straight-chain alkyl group
20 contains less than 15% tertiary and/or quaternary carbon
21 atoms in the remainder of the alkyl group; more preferably,
22 less than 10%; still more preferably, less than 5%; and most
23 preferably, the substantially straight-chain alkyl group
24 contains no tertiary or quaternary carbon atoms in the
25 remainder of the alkyl group.

26

27 The term "oil solubility" means that the additive has a
28 solubility of at least 50 grams per kilogram and preferably
29 at least 100 grams per kilogram at 20°C in a base 10W40
30 lubricating oil.

31

32

33

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01 Methodology

02

03 In the method of the present invention, alkylated alkyl
04 salicylate is overbased with an excess amount of an alkaline
05 earth metal base (e.g., alkaline earth metal oxide,
06 hydroxide or C₁ to C₆ alkoxide) and optionally with carbon
07 dioxide.

08

09 Specifically, in the methods of this invention, alkaline
10 earth metal base is combined with the alkylated alkyl
11 salicylate under conditions wherein the amount of such base
12 employed is that which is in excess of that necessary to
13 neutralize the acidic species on the alkylated alkyl
14 salicylate and optionally carbon dioxide is also employed to
15 further enhance the basicity of the overbased product. Such
16 overbased products are characterized as having a TBN of
17 greater than 0 and preferably no more than about 300.

18

19 The reaction is preferably conducted in an inert diluent
20 under conditions wherein the alkaline earth metal base is
21 incorporated into the alkylated alkyl salicylate.

22 Preferably, the reaction is conducted at a temperature of
23 from about 20°C to about 100°C and is preferably complete
24 within a period of from about 0.2 to about 5 hours. The
25 amount of alkylated alkyl salicylate employed is preferably
26 from about 5 to about 50 weight percent based on the total
27 of diluent and alkylated alkyl salicylate employed and more
28 preferably from about 15 to about 50 weight percent.

29

30 Without being limited to any theory, I believe that the
31 alkaline earth metal base is incorporated through the
32 hydroxyl group of the salicylate and that the carbonyl group
33 of the ester participates in facilitating this
34 incorporation.



01 The amount of alkaline earth metal base which can be
02 practically incorporated into alkylated alkyl salicylate is
03 generally limited to products having a TBN of greater than 0
04 and less than about 100 and preferably less than about 50.
05 While such products are nevertheless overbased products, the
06 preparation of products having a TBN of greater than about
07 100 requires the further use of carbon dioxide. Also,
08 carbon dioxide can be employed but is not necessary in the
09 preparation of overbased compositions having a TBN of from
10 greater than 0 to about 100.

11

12 Preferably, the amount of alkaline earth metal base employed
13 is from about 0.6 to about 2.5 molar equivalents based on
14 the amount of alkylated alkyl salicylate employed. At this
15 range, the alkaline earth metal base is in excess over that
16 which is necessary to neutralize all of the acidic species
17 on the alkylate alkyl salicylate.

18

19 In general, from about 0.1 to about 1.5 molar equivalents of
20 carbon dioxide to the alkaline earth metal base and
21 preferably from about 0.5 to about 1.25 molar equivalents,
22 are then added to the reaction mixture via conventional
23 methods after alkaline earth metal incorporation and the
24 carbonation step is preferably conducted at from about 20°C
25 to about 80°C.

26

27 After reaction completion, the solids are generally removed
28 by conventional means (i.e., filtration, centrifugation,
29 etc.) and the inert diluent solvent can be removed by
30 conventional means such as stripping under reduced pressure.

31

32 When carbon dioxide is not employed, the inert diluent is
33 preferably 2-ethylhexanol and diluent oil but a mixture of
34 an alkanol of from 1 to 3 carbon atoms and an aromatic



01 solvent having a boiling point less than about 150°C can
02 also be employed.

03

04 When carbon dioxide is employed, the inert diluent is
05 preferably a mixture of an alkanol of from 1 to 3 carbon
06 atoms and an aromatic solvent having a boiling point of less
07 than about 150°C.

08

09 Suitable alcohols include methanol, ethanol, n-propanol and
10 iso-propanol. Suitable aromatic solvents having a boiling
11 point of less than about 150°C include, by way of example,
12 benzene, toluene, xylene, chlorobenzene and the like. The
13 diluent preferably comprises from about 5 to about 30 weight
14 percent of the alkanol of from 1 to 3 carbon atoms and from
15 about 95 to about 70 weight percent of the aromatic solvent.
16 A particularly preferred diluent is a mixture methanol and
17 toluene preferably at a weight ratio of 20 to 80.

18

19 Other components can be included in the diluent such as
20 lubricating oil base stock.

21

22 In one preferred embodiment, the diluent does not contain a
23 lubricating oil base stock and, after reaction completion,
24 substantially all diluent is stripped from the overbased
25 product to provide for a fluid product having a viscosity of
26 less than about 1000 cSt at 100°C and preferably less than
27 500 cSt at 100°C.

28

29 In another preferred embodiment, lubricating oil base stock
30 is included during preparation of the overbased product and,
31 after product preparation, the alkanol and aromatic solvent
32 are removed by stripping.

33

34

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01 In still another preferred embodiment, the reaction is
02 conducted in the absence of lubricating oil base stock and,
03 after product preparation, the base stock is added either
04 before or after the alkanol and aromatic solvent are removed
05 by stripping.

06

07 In either of the latter two cases, the resulting composition
08 comprises a concentrate of the overbased alkylated alkyl
09 salicylate in a base stock which is suitable for use in
10 directly formulating a lubricating oil composition. When so
11 employed, the amount of lubricating oil base stock included
12 in the concentrate comprises from about 5 to about 95 weight
13 percent base stock and from about 95 to about 5 weight
14 percent overbased alkylated alkyl salicylate.

15

16 The alkylated alkyl salicylates used in the preparation of
17 overbased alkylated alkyl salicylates can be prepared by
18 methods known in the art such as that described in Deutsche
19 Patentschrift DD 269 619 and DD 272,065 as well as Japanese
20 Patent Application No. 54/160335 which methods employ an
21 excess of alkyl salicylate to the alkylating agent (e.g.,
22 olefin) or an excess of alkylating agent to the alkyl
23 salicylate. The alkylated alkyl salicylates, however, are
24 preferably prepared by the methods described in U.S. Patent
25 Application Serial No. 08/_____,_____ filed concurrently
26 herewith as Attorney Docket No. 005950-367 and entitled
27 "ALKYLATION OF ALKYL SALICYLATE USING A LONG CHAIN CARBON
28 FEED" and which are further described in Example 2 below.

29

30 Preferably, the alkylated alkyl salicylate is alkylated with
31 substantially straight-chain olefins. Particularly
32 preferred alkylating olefins include substantially straight-
33 chain C_{20} - C_{28} olefins, substantially straight-chain C_{20} - C_{24}
34 olefins, and substantially straight-chain C_{24} - C_{28} olefins.



01 Utility

02

03 The oil-soluble, overbased alkylated alkyl salicylate
04 compositions described above are useful lubricating oil
05 additives imparting detergency and dispersancy properties
06 when added to the lubricating oil employed in the crank case
07 of an internal combustion engine as well as an alkaline
08 reserve which is essential to neutralize acidic combustion
09 products produced during engine operation. Such lubricating
10 oil compositions are useful in diesel engines, gasoline
11 engines as well as in marine engines. When employed in this
12 manner, the amount of oil-soluble, neutral and low overbased
13 alkyl methyl salicylate added to the lubricating oil
14 composition ranges from about 0.5 to 40 weight percent of
15 the total lubricant composition although preferably from
16 about 2 to 30 weight percent of the total lubricant
17 composition.

18

19 Such lubricating oil compositions employ a finished
20 lubricating oil which may be single or multigrade.
21 Multigrade lubricating oils are prepared by adding viscosity
22 index (VI) improvers. Typical viscosity index improvers are
23 polyalkyl methacrylates, ethylene, propylene copolymers,
24 styrene-diene copolymers, and the like.

25

26 The lubricating oils used in such compositions may be
27 mineral oils or synthetic oils of viscosity suitable for use
28 in the crank case of an internal combustion engine such as
29 gasoline engines and diesel engines which include marine
30 engines. Crank case lubricating oils ordinarily have a
31 viscosity of about 1300 cSt at 0°F to 24 cSt at 210°F
32 (99°C). The lubricating oils may be derived from synthetic
33 or natural sources. Mineral oils for use as the base oil in
34 the invention includes paraffinic, naphthenic and other oils



01 that are ordinarily used in lubricating oil compositions.
02 Synthetic oils include both hydrocarbon synthetic oils and
03 synthetic esters. Useful synthetic hydrocarbon oils include
04 liquid polymers of α -olefins having the proper viscosity.
05 Especially useful are the hydrogenated liquid oligomers of
06 C_6 to C_{12} alpha olefins such as 1-decene trimer. Likewise,
07 alkylbenzenes of proper viscosity such as didodecyl benzene,
08 can be used. Useful synthetic esters include esters of both
09 monocarboxylic acids and polycarboxylic acids as well as
10 monohydroxy alkenols and polyols. Typical examples are
11 didodecyl adipate, pentaerythritol tetracaproate, di-2-
12 ethylhexyl adipate, dilaurylsebacate and the like. Complex
13 esters prepared from mixtures of mono and dicarboxylic acid
14 and mono and dihydroxy alkanols can also be used.

15

16 Blends of hydrocarbon oils with synthetic oils are also
17 useful. For example, blends of 10 to 25 weight percent
18 hydrogenated 1-decene trimer with 75 to 90 weight percent
19 150 SUS (100°F) mineral oil gives an excellent lubricating
20 oil base.

21

22 Other additives which may be present in the formulation
23 include rust inhibitors, foam inhibitors, corrosion
24 inhibitors, metal deactivators, pour point depressants,
25 anti-oxidants, and a variety of other well-known additives.

26

27 The invention will be illustrated in greater detail by the
28 following specific examples. It is understood that these
29 examples are given by way of illustration only and are not
30 meant to limit the disclosure of the claims to follow.

31

32

EXAMPLES

33

34

This Sheet Has Been Replaced



01 **Example 1 -- Preparation of Alkylated Methyl Salicylate**
02 **Using 1:5 Molar Ratio of Olefin to Methyl**
03 **Salicylate**

04 Methyl salicylate (from Aldrich Chemical Company, Milwaukee,
05 Wisconsin, USA) was alkylated with a C₂₀-C₂₄ olefin carbon
06 feed at a molar ratio of 5:1 of methyl salicylate to carbon
07 feed. In this example, 1802.6 grams of a C₂₀-C₂₄ olefin
08 fraction (available from Chevron Chemical Company, San
09 Ramon, California, USA), was charged to a 5 liter, four-neck
10 oven dry flask. 2457.5 grams of methyl salicylate followed
11 by 591.3 grams of AMBERLYST®36 sulfonic acid resin
12 (available from Rohm and Haas, Philadelphia, Pennsylvania,
13 USA) were next charged to the flask. The flask was then
14 equipped with a stirrer, temperature probe with controller,
15 reflux condenser and a nitrogen blanket.

16 The reaction mixture was heated to a temperature of 125°C
17 over a period of 50 minutes and held at that temperature for
18 approximately 48 hours. After 48 hours, about 94.2%
19 conversion of the methyl salicylate to alkyl methyl
20 salicylate had occurred. The reaction mixture was cooled
21 with stirring overnight to a temperature of about 50°C.
22

23 The crude alkyl methyl salicylate was removed from the
24 reaction flask by using a gas dispersion tube and pulling it
25 into a four liter flask under vacuum. The catalyst remained
26 in the reaction flask. Product remaining on the catalyst
27 was removed by rinsing the contents of the flask with
28 approximately 400 ml portions of toluene while stirring,
29 followed by pulling the toluene and crude product into a two
30 liter flask through a gas dispersion tube under vacuum.
31 This rinsing/pulling procedure was repeated additional three
32 times. The toluene recovered in this procedure was stripped
33 on a rotovap at a temperature of approximately 95°C to 100°C
34



01 under vacuum ($\sim$ 25 mm of Hg vacuum) and the resulting
02 stripped product was combined with the recovered crude
03 alkylated methyl salicylate.

04
05 The combined crude alkylated methyl salicylate was then
06 stripped at a temperature of about 130°C at a pressure of
07 approximately 1 to 10 mm of mercury. Further stripping was
08 conducted at a temperature of about 185°C to 191°C at a
09 pressure of approximately 1 to 10 mm of mercury. Product
10 analysis indicated that about 94.7 weight percent of the
11 methyl salicylate was alkylated.

12
13 **Example 2 -- Preparation of Alkyl Methyl Salicylate Using**
14 **1:1 Molar Ratio of Olefin to Methyl**
15 **Salicylate**

16 Methyl salicylate commercially obtained from Aldrich
17 Chemical Company, Milwaukee, Wisconsin, USA was alkylated
18 using a long chain carbon feed. In this example, 617.9
19 grams (2.0 moles) of a C₂₀-C₂₄ alpha olefin fraction
20 (available from Chevron Chemical Company, San Ramon,
21 California, USA), was charged to a 2 liter, three-neck oven
22 dry flask. 304.3 grams (2 moles) of methyl salicylate,
23 followed by 150 grams of AMBERLYST®36 (a solid acidic
24 sulfonic acid resin catalyst commercially available from
25 Rohm & Haas, Philadelphia, Pennsylvania, USA), were next
26 charged to the flask. The flask was then equipped with a
27 stirrer, temperature probe with controller, reflux condenser
28 and a nitrogen blanket.

29
30 The reaction mixture was heated to a temperature of 135°C
31 over a period of 25 minutes and held at that temperature for
32 approximately 61 hours while periodically removing aliquots
33 to check reaction completion. After 61 hours, the recovered
34

product was analyzed for its components which analysis is reported in Table I below:

TABLE I COMPONENTS IN RECOVERED ALKYLATED METHYL SALICYLATE	
COMPONENT	WEIGHT PERCENT
Salicylic acid	1.5%
Olefin	6.5%
Alkyl methyl salicylate	87.5%
Methyl salicylate	4.5%

The product was filtered through a sintered glass filter. The filtered alkyl methyl salicylate was heated to a temperature of 210°C over a period of about 45 minutes and then stripped under vacuum of about 1 to 10 mm of Hg was applied. These stripping conditions were maintained for about 30 minutes. The stripped product was next cooled to 150°C and the vacuum broken with a nitrogen stream. 739.9 grams of product was recovered. Analysis of this product is set forth in Table II below:

TABLE II COMPONENTS IN RECOVERED AND STRIPPED ALKYLATED METHYL SALICYLATE	
COMPONENT	WEIGHT PERCENT
Salicylic acid	0.1%
Olefin	4.7%
Alky methyl salicylate	95.2%

This Sheet Has Been Replaced



01 **Example 3 -- Preparation of Overbased Alkyl Methyl**
02 **Salicylate Additive Composition in the**
03 **Absence of Carbon Dioxide**

04 Alkyl methyl salicylate produced in the manner similar to
05 either Example 1 or 2 above is overbased with an excess of
06 calcium hydroxide. In this example, 100 grams of C₂₀-C₂₄
07 alkylated methyl salicylate is combined into approximately
08 500 ml of 2-ethylhexanol at room temperature. About 20
09 grams of lime are added to the solution and the solution is
10 maintained at about 30°C for about 2 hours. Afterwards, the
11 2-ethylhexanol diluent is removed by stripping to provide
12 for an overbased alkylated alkyl salicylate having a TBN of
13 greater than zero and less than about 100.

14

15 **Example 4 -- Preparation of Overbased Alkyl Methyl**
16 **Salicylate Additive Composition Containing**
17 **Carbon Dioxide**

18 To a 2 liter, 4-neck round bottom flask were added 100 grams
19 of methanol, 480 grams of xylene, and 90 grams of
20 Mississippi Lime (Mississippi Lime Company, Ste. Genevieve,
21 Missouri, USA). The resulting system was stirred for 10
22 minutes. Afterwards, 266 grams of alkyl methyl salicylate,
23 prepared in a manner similar to that of Examples 1 and 2,
24 was slowly added to the system, over about a 1.5 hour
25 period, while maintaining a maximum temperature of 31°C.

26

27 At this point, carbonation was initiated and approximately
28 28 grams of carbon dioxide were added at the following
29 rates:

30

31 17.5 grams CO₂ at 0.295 grams/minute
32 2.4 grams CO₂ at 0.224 grams/minute
33 2.8 grams CO₂ at 0.183 grams/minute
34 2.8 grams CO₂ at 0.140 grams/minute
2.8 grams CO₂ at 0.061 grams/minute

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01 Upon completion of the carbonation step, the system was
02 heated to 93°C over a 2 hour period and then heated to
03 132°C over a 30 minute period. At this point, 155 grams of
04 diluent oil, CitCon 100N, was added and the system heated to
05 204°C over 1.5 hours under vacuum to strip of the xylene.
06 The resulting solution was then filtered over Celite™
07 (diatomaceous earth available from Manville Corporation) so
08 as to provide an overbased carbon dioxide containing alkyl
09 methyl salicylate additive composition having a TBN of about
10 182 and a viscosity of 100°C of about 19 cSt.
11

12 Proton nuclear magnetic resonance spectroscopy (¹H-nmr) and
13 infrared spectroscopy of the resulting composition indicated
14 the retention of the methyl ester in the overbased product.
15

16 **Example 5 -- Dispersion Test**

17 Overbased Alkylated alkyl salicylate prepared in Example 4
18 above was tested for dispersancy in the following dispersion
19 test. In this test, the dispersant ability of the
20 formulated lubricating oil composition is obtained by
21 conducting chromatography on paper of a mixture of the
22 lubricating oil composition to be tested and an artificial
23 sludge under the following conditions:

24	Spot No. 1	Ambient temperature without water
25	Spot No. 2	10 minutes at 200°C without water
26	Spot No. 3	10 minutes at 250°C without water
27	Spot No. 4	Ambient temperature with 1% water
27	Spot No. 5	10 minutes at 200°C with 1% water
28	Spot No. 6	10 minutes at 250°C with 1% water

29 The spots are rated after 48 hours. For each spot, the
30 diameters of diffusion of soot (d) and of the oil (D) are
31 measured and the ratio

32
$$\frac{d}{D} \times 100$$

33 D
34

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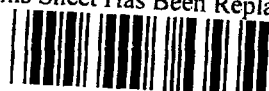

01 is calculated. The dispersancy of the oil over a variety of
02 conditions is obtained from the sum of the six spot ratings.
03 Oils having values of greater than about 250 are considered
04 to have dispersant properties and are compared to reference
05 oils, i.e., an oil having 23.4 weight percent of
06 commercially available salicylate under otherwise identical
07 parameters.

08
09 The lubricating oil composition was prepared by combining 22
10 weight percent of an overbased alkylated alkyl salicylate
11 similar to that of Example 4 above, 0.67 weight percent of a
12 zinc dithiophosphate and 1.60 weight percent of an alkenyl
13 succinimide to a SAE 30 oil. The resulting composition has
14 1.505 weight percent calcium, 0.080 weight percent zinc;
15 0.050 weight percent phosphorus; 0.03 weight percent
16 nitrogen; a TBN of about 40.2; and a viscosity of 100°C of
17 11.8 cSt.

18
19 20 grams of this test composition were then combined with 5
20 grams of sludge containing 2% of carbonaceous material. The
21 mixture is then homogenized. In the samples containing
22 water, 1% water (250 μ l) is added to the composition prior
23 to homogenizing.

24
25 The freshly homogenized test lubricating oil composition (20
26 μ l of each but done in duplicate) are syringed onto 2
27 separate sheets of paper using a 100 μ l syringe. The heated
28 samples are first incubated in a heating bath at the
29 indicated temperature for 10 minutes before application.

30
31 The papers are stored in the horizontal position for 48
32 hours at a temperature of from about 20° to about 25°C.
33 Storage is conducted under conditions to shelter the papers
34 from dust.



01 After 48 hours, the spots should be circular and the zone of
02 dispersion of the soot (d) as well as the zone of the
03 dispersion of the oil (D) are measured. For additives
04 providing good dispersancy, the sum of the six values of d/D
05 x 100 should be at least 250. In the present case, the sum
06 was 312. This indicates that the salicylates of this
07 invention possess dispersant properties. Additionally,
08 comparison to reference oil indicates similar properties,
09 i.e., the sum of these 6 spots for the reference oil was
10 332.

11

12 **Example 6 -- Hydrolytic Stability Test**

13 Overbased alkylated alkyl salicylate prepared in Example 4
14 was tested for its hydrolytic stability. The test comprises
15 preparing a formulated lubricating oil composition wherein
16 the TBN is derived primarily from the overbased alkylated
17 alkyl salicylate composition. In the present case, the
18 tested lubricant compositions were formulated with 1 weight
19 percent of a succinimide dispersant and 8 mmoles of a ZnDTP
20 containing secondary alkyl groups in a base stock which was
21 additionally formulated with 22 weight percent of the
22 alkylated alkyl salicylate so as to provide for a TBN of
23 about 40.

24

25 In this test, 98 grams of the formulated lubricating oil
26 composition and 2 grams of distilled water are combined and
27 sealed in a pressure type beverage bottle. The bottle is
28 rotated end over end for about 70 hours in a convention oven
29 maintained at about 93°C. The bottles are then cooled to
30 room temperature and the contents thereof are poured into a
31 centrifuge tube and spun at 10,000 rotations per minute for
32 about 60 minutes at room temperature. The TBN of the oil
33 layer is then determined and loss of TBN relates to the
34 hydrolytic stability of the lubricant oil composition -- the



01 greater the loss of TBN the less hydrolytically stable the
02 lubricant oil composition was.

03

04 In this test, the resulting TBN loss was 3% which reflected
05 that these compositions were hydrolytically stable.

06 Additionally, the amount of filtered deposits was 0.09%
07 which indicated little formation of solid residues upon
08 exposure to water.

09

10 While the invention has been described in terms of various
11 preferred embodiments, the skilled artisan will appreciate
12 that various modifications, substitutions, omissions, and
13 changes may be made without departing from the spirit
14 thereof. Accordingly, it is intended that the scope of this
15 invention be limited solely by the scope of the following
16 claims, including equivalents thereof.

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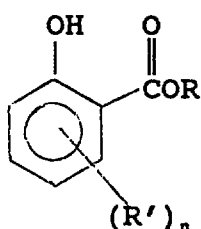
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WHAT IS CLAIMED IS:

1. A lubricating oil soluble, overbased alkylated alkyl salicylate composition wherein said composition has a TBN of from greater than 0 to about 300 and further wherein said alkylated alkyl salicylate has the formula prior to overbasing of:



- wherein R is alkyl of from 1 to about 6 carbon atoms; R' is an alkyl group of from about 15 to 50 carbon atom; and n is an integer of from 1 to 2.
2. The composition according to Claim 1 wherein R is methyl and R' is an alkyl group of from about 20 to about 50 carbon atoms.
 3. The composition according to Claim 1 wherein R' is a mixture of C₂₀-C₂₄ alkyl groups.
 4. The composition according to Claim 1 wherein said overbased alkylated alkyl salicylate has a TBN of from greater than 0 to about 100.
 5. The composition according to Claim 1 wherein said overbased alkylated alkyl salicylate has a TBN of from greater than about 100 to about 300.
 6. The composition according to Claim 1 which further comprises from about 5 to 95 weight percent of a diluent oil.

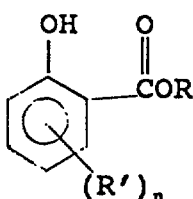
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01 7. A lubricating oil soluble, overbased alkylated alkyl
02 salicylate composition which is prepared by the process
03 which comprises:

04 (a) combining into a diluent from about 15 to about 50
05 weight percent of an alkylated alkyl salicylate based
06 on the total weight of the alkylated alkyl
07 salicylate/diluent composition wherein said alkylated
08 alkyl salicylate is of the formula



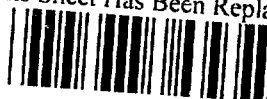
14 where R is alkyl of from 1 to about 6 carbon atoms; R'
15 is an alkyl group of from about 15 to about 50 carbon
16 atom; and n is an integer of from 1 to 2;

17 (b) combining a sufficient amount of an alkaline earth
18 metal base into the composition produced in (a) above
19 under conditions wherein the amount of alkaline earth
20 metal is incorporated into the salicylate in excess of
21 that necessary to neutralize the alkylated alkyl
22 salicylate; and

23
24 (c) optionally contacting from about 0.1 to about 1.5
25 molar equivalents of carbon dioxide based on each molar
26 equivalent of alkylated alkyl salicylic acid under
27 conditions wherein carbon dioxide is incorporated into
28 the composition wherein the overbased composition has a
29 TBN of from greater than 0 to about 300.

30
31 8. The composition according to Claim 7 wherein the
32 alkaline earth metal base is selected from the group
33 consisting of an alkaline earth metal oxide, hydroxide,
34 and C₁ to C₆ alkoxide.

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- 01 9. The composition accordingly to Claim 8 wherein the
02 alkaline earth metal base is calcium hydroxide.
03
- 04 10. The composition according to Claim 7 wherein R is
05 methyl and R' is an alkyl group of from about 20 to
06 about 50 carbon atoms.
07
- 08 11. The composition according to Claim 10 wherein R' is a
09 mixture of C₂₀-C₂₄ alkyl groups.
10
- 11 12. The composition according to Claim 7 wherein said
12 overbased alkylated alkyl salicylate is prepared in the
13 absence of carbon dioxide wherein said composition has
14 a TBN of greater than 0 and less than 100.
15
- 16 13. The composition according to Claim 12 wherein said
17 overbased alkylated alkyl salicylate has a TBN of
18 greater than 0 and less than 50.
19
- 20 14. The composition according to Claim 7 wherein said
21 overbased alkylated alkyl salicylate is prepared using
22 carbon dioxide.
23
- 24 15. The composition according to Claim 7 which further
25 comprises from about 5 to 95 weight percent of a
26 diluent oil.
27
- 28 16. A lubricating oil composition comprising an oil of
29 lubricating viscosity and from about 2 to about 30
30 weight percent of an overbased alkylated alkyl
31 salicylate additive composition according to Claim 1.
32
- 33 17. A lubricating oil composition comprising an oil of
34 lubricating viscosity and from about 2 to about 30





- 01 weight percent of an overbased alkylated alkyl
02 salicylate additive composition according to Claim 2.
03
- 04 18. A lubricating oil composition comprising an oil of
05 lubricating viscosity and from about 2 to about 30
06 weight percent of an overbased alkylated alkyl
07 salicylate additive composition according to Claim 3.
08
- 09 19. A lubricating oil composition comprising an oil of
10 lubricating viscosity and from about 2 to about 30
11 weight percent of an overbased alkylated alkyl
12 salicylate additive composition according to Claim 4.
13
- 14 20. A lubricating oil composition comprising an oil of
15 lubricating viscosity and from about 2 to about 30
16 weight percent of an overbased alkylated alkyl
17 salicylate additive composition according to Claim 5.
18
- 19 21. A lubricating oil composition comprising an oil of
20 lubricating viscosity and from about 2 to about 30
21 weight percent of an overbased alkylated alkyl
22 salicylate additive composition according to Claim 6.
23
- 24 22. A lubricating oil composition comprising an oil of
25 lubricating viscosity and from about 2 to about 30
26 weight percent of an overbased alkylated alkyl
27 salicylate additive composition according to Claim 7.
28
- 29 23. A lubricating oil composition comprising an oil of
30 lubricating viscosity and from about 2 to about 30
31 weight percent of an overbased alkylated alkyl
32 salicylate additive composition according to Claim 8.
33
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- 01 24. A lubricating oil composition comprising an oil of
02 lubricating viscosity and from about 2 to about 30
03 weight percent of an overbased alkylated alkyl
04 salicylate additive composition according to Claim 9.
05
- 06 25. A lubricating oil composition comprising an oil of
07 lubricating viscosity and from about 2 to about 30
08 weight percent of an overbased alkylated alkyl
09 salicylate additive composition according to Claim 10.
10
- 11 26. A lubricating oil composition comprising an oil of
12 lubricating viscosity and from about 2 to about 30
13 weight percent of an overbased alkylated alkyl
14 salicylate additive composition according to Claim 11.
15
- 16 27. A lubricating oil composition comprising an oil of
17 lubricating viscosity and from about 2 to about 30
18 weight percent of an overbased alkylated alkyl
19 salicylate additive composition according to Claim 12.
20
- 21 28. A lubricating oil composition comprising an oil of
22 lubricating viscosity and from about 2 to about 30
23 weight percent of an overbased alkylated alkyl
24 salicylate additive composition according to Claim 13.
25
- 26 29. A lubricating oil composition comprising an oil of
27 lubricating viscosity and from about 2 to about 30
28 weight percent of an overbased alkylated alkyl
29 salicylate additive composition according to Claim 14.
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ABSTRACT OF THE DISCLOSURE

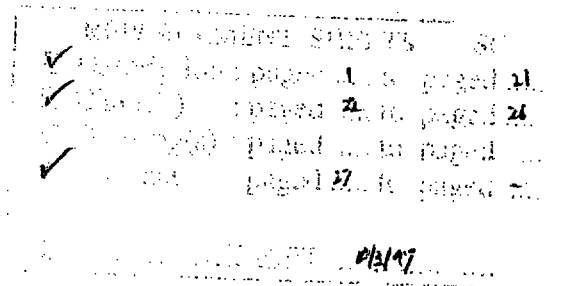
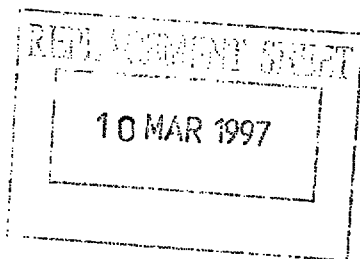
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This invention is directed to overbased alkyl alkyl salicylate which are useful additives for lubricating oil compositions. In particular, the compositions, of this invention impart detergency and discrepancy to the lubricating oil composition as well as provide for alkalinity reserve.

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OVERBASED ALKYLATED ALKYL SALICYLATES

BACKGROUND OF THE INVENTION

Field of the Invention

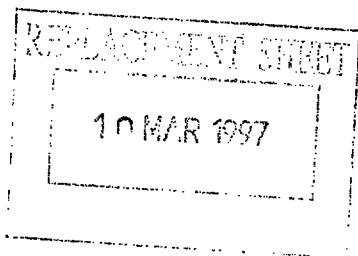
This invention is directed to overbased alkylated alkyl salicylates which overbased products are suitable for use in lubricating oil compositions used in internal combustion engines. In particular, these additives impart water tolerance, thermal stability, detergency, compatibility and good oxidation performance in such lubricating oil compositions.

State of the Art

Overbased alkylated salicylates are a class of lubricating oil detergents known to impart improved performance (detergency, water tolerance, thermal stability, antioxidancy) to lubricating oil compositions used for lubrication of internal combustion engines.

Overbased salicylates are prepared by overbasing the corresponding alkylated salicylic acids which, in turn, are typically prepared by first alkylating phenol to form alkylphenol followed by carboxylation via the Kolbe-Schmitt reaction to provide for alkylated salicylic acid. The alkyl group is typically a long chain alkyl group of greater than about 14 carbon atoms so as to impart oil solubility.

One problem encountered with this synthetic scheme when a substantially linear alkylation feed is employed is that not all of the long chain alkylphenol is readily carboxylated via the Kolbe-Schmitt reaction. Specifically, conventional alkylation of phenol with a substantially linear alkylation feed provides for approximately a 50:50 mixture of ortho-

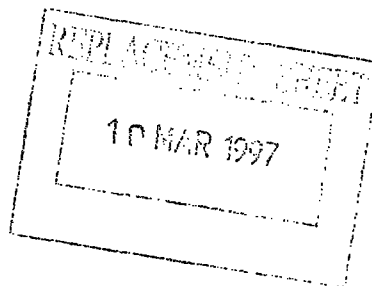


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alkylphenol and para-alkylphenol. While the Kolbe-Schmitt reaction readily carboxylates the resulting long chain para-alkylphenol, the resulting long chain ortho-alkylphenol is less reactive and only about 70 percent of total amount of the alkylphenol derived from a substantially linear alkylation feed is typically converted to alkylated salicylic acid during this reaction.

One method of circumventing this problem is to alkylate an alkyl salicylate (e.g., methyl salicylate) and then subject the resulting alkylated alkyl salicylate to hydrolysis so as to provide for the alkylated salicylic acid. Methods of alkylating alkyl salicylates are disclosed in U.S. Patent Application Serial No. 08/_____ filed concurrently herewith as Attorney Docket No. 005950-367 and entitled "ALKYLATION OF ALKYL SALICYLATE USING A LONG CHAIN CARBON FEED" which application is incorporated herein by reference in its entirety.

This latter synthetic scheme involves formation of an alkyl salicylate, alkylation of the alkyl salicylate to form an alkylated alkyl salicylate, followed by hydrolysis to form the alkylated salicylic acid. Hydrolysis of the alkylated alkyl salicylate to form alkylated salicylic acid was perceived necessary to later formation of overbased products since the carboxyl (-COOH) group was deemed to be an essential component during overbasing. Specifically, overbased products are prepared by the addition of excess basic metal (i.e., greater than that required to neutralize all of the acidic species on the salicylic acid) optionally using carbon dioxide and it was considered that the carboxyl group played an essential role in the ability of the alkylated salicylic acid to incorporate excess basic metal and carbon dioxide presumably via chelation.



This invention is directed, in part, to the discovery that alkylated alkyl salicylates can be overbased without hydrolysis of the ester functionality to provide for overbased lubricating oil additives suitable for use in lubricating oil compositions. This discovery is particularly surprising in view of the fact that the overbased products of this invention lack carboxyl ($-\text{COOH}$) functionality but, rather, possess an ester ($-\text{COOR}$) functionality (R being alkyl of from 1 to 6 carbon atoms).

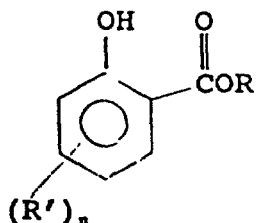
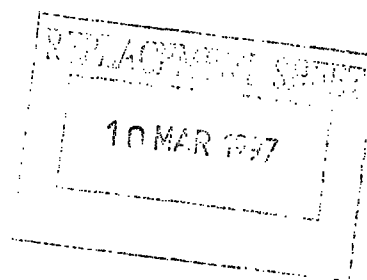
SUMMARY OF THE INVENTION

This invention is directed, in part, on the discovery that alkylated alkyl salicylates can be directly overbased without hydrolysis of the ester and such overbased products provide for a new class of lubricating oil additives, which exhibit detergency, a source of alkaline reserve, etc. in the finished lubricating oil composition.

Accordingly, in one of its composition aspects, this invention is directed to a lubricating oil soluble, overbased alkylated alkyl salicylate additive composition having a TBN of from greater than 0 to about 300.

In another of its composition aspects, this invention is directed to a lubricating oil soluble, overbased alkylated alkyl salicylate composition which is prepared by the process which comprises:

- (a) combining into a diluent from about 15 to about 50 weight percent of an alkylated alkyl salicylate based on the total weight of the alkylated alkyl salicylate/diluent composition wherein said alkylated alkyl salicylate is of the formula



where R is alkyl of from 1 to about 6 carbon atoms; R' is an alkyl group of from about 15 to about 50 carbon atom; and n is an integer from 1 to 2:

(b) combining a sufficient amount of an alkaline earth metal base into the composition produced in (a) above under conditions wherein the amount of alkaline earth metal is incorporated into the salicylate in excess of that necessary to neutralize the alkylated alkyl salicylate; and

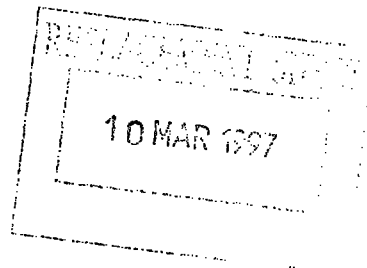
(c) optionally contacting from about 0.1 to about 1.5 molar equivalents of carbon dioxide based on each molar equivalent of alkylated alkyl salicylic acid under conditions wherein carbon dioxide is incorporated into the composition

wherein the overbased composition has a TBN of from greater than 0 to about 300.

In still another of its composition aspects, this invention is directed to a lubricating oil composition comprising an oil of lubricating viscosity and from about 2 to about 30 weight percent of an overbased alkylated alkyl salicylate additive composition having a TBN of from greater than 0 to about 300.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

This invention is directed to novel overbased alkylated alkyl salicylate compositions which are useful additives for lubricating oil compositions. However, prior to discussing



this invention in detail, the following terms will first be defined:

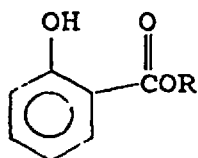
Definitions

As used herein, the term "Total Base Number" or "TBN" refers to the amount of base equivalent to milligrams of KOH in 1 gram of additive. Thus, higher TBN numbers reflect more alkaline products and therefore a greater alkalinity reserve. The Total Base Number for an additive composition is readily determined by ASTM test method number D2896 or other equivalent methods.

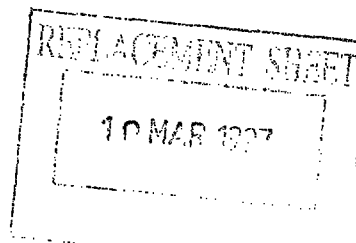
The term "alkaline earth metal" or "Group II metal" means calcium, barium, magnesium, and strontium. Preferably, the Group II metal is selected from the group consisting of calcium, magnesium, barium, and mixtures thereof. Most preferably, the Group II metal is calcium.

The term "alkaline earth metal base" refers to basic alkaline earth metal materials suitable for use in preparing overbased alkylated alkyl salicylates and, include by way of example, alkaline earth metal oxides, hydroxides and C₁ to C₆ alkoxides.

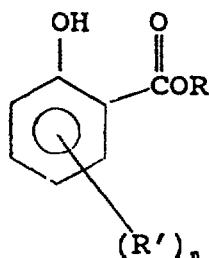
The term "alkyl salicylates" refers to compounds of the formula:



wherein R is an alkyl group of from 1 to 6 carbon atoms. Preferably, R is an alkyl group of from 1 to 3 carbon atoms and most preferably R is methyl.



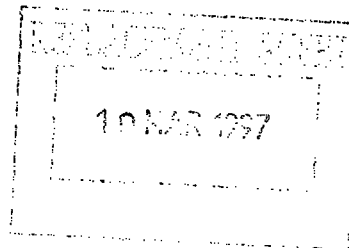
The term "alkylated alkyl salicylate" refers to alkyl salicylates which have been alkylated with a long chain carbon feed which alkylated products can be represented by the formula:



where R is as defined above; R' is an alkyl group of from about 15 to 50 carbon atoms; and n is an integer of from 1 to 2 and is preferably 1. In a preferred embodiment, the amount of dialkylation in the product is maintained to about 5% or less.

The term "overbased alkylated alkyl salicylate compositions" refers to compositions prepared by reacting an alkylated alkyl salicylate with an amount of alkaline earth metal base in excess of that necessary to neutralize the acidic species on the alkylated alkyl salicylate and optionally with carbon dioxide. Such overbased products are characterized as having a TBN of greater than 0 and preferably no more than about 300.

The overbased alkylated alkyl salicylate compositions described herein can contain diluent and the term "overbased alkylated alkyl salicylate compositions" is meant to include compositions containing such diluent. Typically, such compositions are manufactured to contain some diluent and, after manufacture, the diluent can be removed, replaced or additional amounts of diluent can be added to provide for an additive composition preferably having from 0 to about 40 weight percent diluent. As such, these additive compositions contain concentrated amounts of the overbased



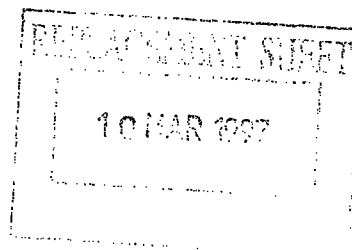
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alkylated alkyl salicylate of which only a small amount is added together with other additives to a lubricating oil so as to provide for a fully formulated lubricant composition suitable for use in an internal combustion engine.

The term "substantially straight-chain alkyl group" means an alkyl group which is attached to the benzene ring of the alkyl salicylate through a secondary, tertiary or quaternary carbon atom and which contains minimal branching in the remainder of the carbon atoms of the alkyl group (i.e., less than 20% of the remaining carbon atoms are tertiary and/or quaternary carbon atoms in the molecular structure of the alkyl group). Suitable substantially straight-chain alkyl groups include, for example, 1-hexadecyl $-\text{[CH}_2(\text{CH}_2)_{14}\text{CH}_3]$ (0% of the carbon atoms are tertiary or quaternary carbon atoms), 4-methyl-1-hexadecyl $-\text{[CH}_2(\text{CH}_2)_2\text{CHCH}_3(\text{CH}_2)_{11}\text{CH}_3]$ (<7% of the carbons are branched), etc.

Preferably, the substantially straight-chain alkyl group contains less than 15% tertiary and/or quaternary carbon atoms in the remainder of the alkyl group; more preferably, less than 10%; still more preferably, less than 5%; and most preferably, the substantially straight-chain alkyl group contains no tertiary or quaternary carbon atoms in the remainder of the alkyl group.

The term "oil solubility" means that the additive has a solubility of at least 50 grams per kilogram and preferably at least 100 grams per kilogram at 20°C in a base 10W40 lubricating oil.



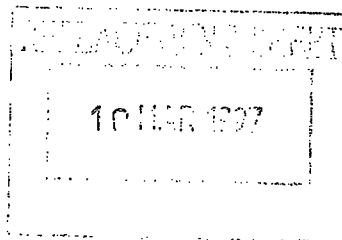
Methodology

In the method of the present invention, alkylated alkyl salicylate is overbased with an excess amount of an alkaline earth metal base (e.g., alkaline earth metal oxide, hydroxide or C_1 to C_6 alkoxide) and optionally with carbon dioxide.

Specifically, in the methods of this invention, alkaline earth metal base is combined with the alkylated alkyl salicylate under conditions wherein the amount of such base employed is that which is in excess of that necessary to neutralize the acidic species on the alkylated alkyl salicylate and optionally carbon dioxide is also employed to further enhance the basicity of the overbased product. Such overbased products are characterized as having a TBN of greater than 0 and preferably no more than about 300.

The reaction is preferably conducted in an inert diluent under conditions wherein the alkaline earth metal base is incorporated into the alkylated alkyl salicylate. Preferably, the reaction is conducted at a temperature of from about 20°C to about 100°C and is preferably complete within a period of from about 0.2 to about 5 hours. The amount of alkylated alkyl salicylate employed is preferably from about 5 to about 50 weight percent based on the total of diluent and alkylated alkyl salicylate employed and more preferably from about 15 to about 50 weight percent.

Without being limited to any theory, I believe that the alkaline earth metal base is incorporated through the hydroxyl group of the salicylate and that the carbonyl group of the ester participates in facilitating this incorporation.



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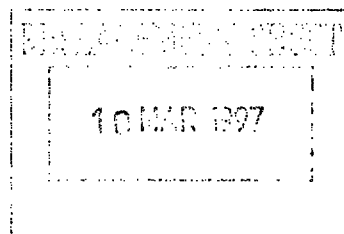
The amount of alkaline earth metal base which can be practically incorporated into alkylated alkyl salicylate is generally limited to products having a TBN of greater than 0 and less than about 100 and preferably less than about 50. While such products are nevertheless overbased products, the preparation of products having a TBN of greater than about 100 requires the further use of carbon dioxide. Also, carbon dioxide can be employed but is not necessary in the preparation of overbased compositions having a TBN of from greater than 0 to about 100.

Preferably, the amount of alkaline earth metal base employed is from about 0.6 to about 2.5 molar equivalents based on the amount of alkylated alkyl salicylate employed. At this range, the alkaline earth metal base is in excess over that which is necessary to neutralize all of the acidic species on the alkylate alkyl salicylate.

In general, from about 0.1 to about 1.5 molar equivalents of carbon dioxide to the alkaline earth metal base and preferably from about 0.5 to about 1.25 molar equivalents, are then added to the reaction mixture via conventional methods after alkaline earth metal incorporation and the carbonation step is preferably conducted at from about 20°C to about 80°C.

After reaction completion, the solids are generally removed by conventional means (i.e., filtration, centrifugation, etc.) and the inert diluent solvent can be removed by conventional means such as stripping under reduced pressure.

When carbon dioxide is not employed, the inert diluent is preferably 2-ethylhexanol and diluent oil but a mixture of an alkanol of from 1 to 3 carbon atoms and an aromatic



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solvent having a boiling point less than about 150°C can also be employed.

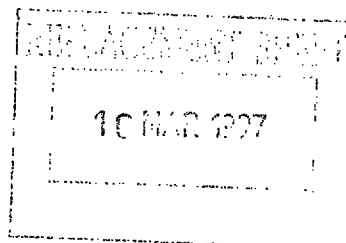
When carbon dioxide is employed, the inert diluent is preferably a mixture of an alkanol of from 1 to 3 carbon atoms and an aromatic solvent having a boiling point of less than about 150°C.

Suitable alcohols include methanol, ethanol, n-propanol and iso-propanol. Suitable aromatic solvents having a boiling point of less than about 150°C include, by way of example, benzene, toluene, xylene, chlorobenzene and the like. The diluent preferably comprises from about 5 to about 30 weight percent of the alkanol of from 1 to 3 carbon atoms and from about 95 to about 70 weight percent of the aromatic solvent. A particularly preferred diluent is a mixture methanol and toluene preferably at a weight ratio of 20 to 80.

Other components can be included in the diluent such as lubricating oil base stock.

In one preferred embodiment, the diluent does not contain a lubricating oil base stock and, after reaction completion, substantially all diluent is stripped from the overbased product to provide for a fluid product having a viscosity of less than about 1000 cSt at 100°C and preferably less than 500 cSt at 100°C.

In another preferred embodiment, lubricating oil base stock is included during preparation of the overbased product and, after product preparation, the alkanol and aromatic solvent are removed by stripping.

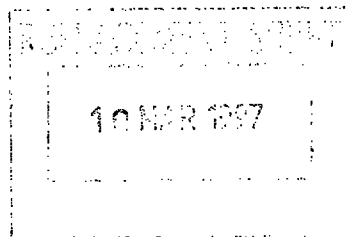


In still another preferred embodiment, the reaction is conducted in the absence of lubricating oil base stock and, after product preparation, the base stock is added either before or after the alkanol and aromatic solvent are removed by stripping.

In either of the latter two cases, the resulting composition comprises a concentrate of the overbased alkylated alkyl salicylate in a base stock which is suitable for use in directly formulating a lubricating oil composition. When so employed, the amount of lubricating oil base stock included in the concentrate comprises from about 5 to about 95 weight percent base stock and from about 95 to about 5 weight percent overbased alkylated alkyl salicylate.

The alkylated alkyl salicylates used in the preparation of overbased alkylated alkyl salicylates can be prepared by methods known in the art such as that described in Deutsche Patentschrift DD 269 619 and DD 272,065 as well as Japanese Patent Application No. 54/160335 which methods employ an excess of alkyl salicylate to the alkylating agent (e.g., olefin) or an excess of alkylating agent to the alkyl salicylate. The alkylated alkyl salicylates, however, are preferably prepared by the methods described in U.S. Patent Application Serial No. 08/_____, filed concurrently herewith as Attorney Docket No. 005950-367 and entitled "ALKYLATION OF ALKYL SALICYLATE USING A LONG CHAIN CARBON FEED" and which are further described in Example 2 below.

Preferably, the alkylated alkyl salicylate is alkylated with substantially straight-chain olefins. Particularly preferred alkylating olefins include substantially straight-chain C_{20} - C_{28} olefins, substantially straight-chain C_{20} - C_{24} olefins, and substantially straight-chain C_{24} - C_{28} olefins.

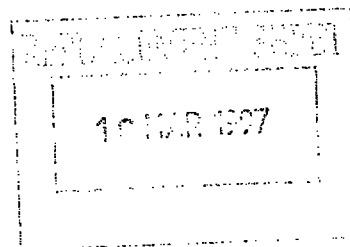


Utility

The oil-soluble, overbased alkylated alkyl salicylate compositions described above are useful lubricating oil additives imparting detergency and dispersancy properties when added to the lubricating oil employed in the crank case of an internal combustion engine as well as an alkaline reserve which is essential to neutralize acidic combustion products produced during engine operation. Such lubricating oil compositions are useful in diesel engines, gasoline engines as well as in marine engines. When employed in this manner, the amount of oil-soluble, neutral and low overbased alkyl methyl salicylate added to the lubricating oil composition ranges from about 0.5 to 40 weight percent of the total lubricant composition although preferably from about 2 to 30 weight percent of the total lubricant composition.

Such lubricating oil compositions employ a finished lubricating oil which may be single or multigrade. Multigrade lubricating oils are prepared by adding viscosity index (VI) improvers. Typical viscosity index improvers are polyalkyl methacrylates, ethylene, propylene copolymers, styrene-diene copolymers, and the like.

The lubricating oils used in such compositions may be mineral oils or synthetic oils of viscosity suitable for use in the crank case of an internal combustion engine such as gasoline engines and diesel engines which include marine engines. Crank case lubricating oils ordinarily have a viscosity of about 1300 cSt at 0°F to 24 cSt at 210°F (99°C). The lubricating oils may be derived from synthetic or natural sources. Mineral oils for use as the base oil in the invention includes paraffinic, naphthenic and other oils



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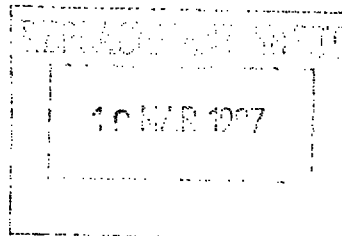
that are ordinarily used in lubricating oil compositions. Synthetic oils include both hydrocarbon synthetic oils and synthetic esters. Useful synthetic hydrocarbon oils include liquid polymers of α -olefins having the proper viscosity. Especially useful are the hydrogenated liquid oligomers of C_6 to C_{12} alpha olefins such as 1-decene trimer. Likewise, alkylbenzenes of proper viscosity such as didodecyl benzene, can be used. Useful synthetic esters include esters of both monocarboxylic acids and polycarboxylic acids as well as monohydroxy alkenols and polyols. Typical examples are didodecyl adipate, pentaerythritol tetracaprate, di-2-ethylhexyl adipate, dilaurylsebacate and the like. Complex esters prepared from mixtures of mono and dicarboxylic acid and mono and dihydroxy alkanols can also be used.

Blends of hydrocarbon oils with synthetic oils are also useful. For example, blends of 10 to 25 weight percent hydrogenated 1-decene trimer with 75 to 90 weight percent 150 SUS (100°F) mineral oil gives an excellent lubricating oil base.

Other additives which may be present in the formulation include rust inhibitors, foam inhibitors, corrosion inhibitors, metal deactivators, pour point depressants, anti-oxidants, and a variety of other well-known additives.

The invention will be illustrated in greater detail by the following specific examples. It is understood that these examples are given by way of illustration only and are not meant to limit the disclosure of the claims to follow.

EXAMPLES

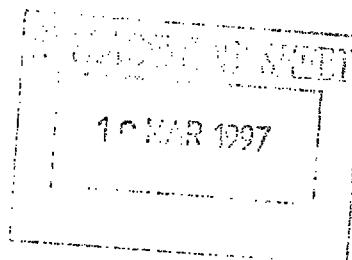


**Example 1 -- Preparation of Alkylated Methyl Salicylate
Using 1:5 Molar Ratio of Olefin to Methyl
Salicylate**

Methyl salicylate (from Aldrich Chemical Company, Milwaukee, Wisconsin, USA) was alkylated with a C_{20} - C_{24} olefin carbon feed at a molar ratio of 5:1 of methyl salicylate to carbon feed. In this example, 1802.6 grams of a C_{20} - C_{24} olefin fraction (available from Chevron Chemical Company, San Ramon, California, USA), was charged to a 5 liter, four-neck oven dry flask. 2457.5 grams of methyl salicylate followed by 591.3 grams of AMBERLYST®36 sulfonic acid resin (available from Rohm and Haas, Philadelphia, Pennsylvania, USA) were next charged to the flask. The flask was then equipped with a stirrer, temperature probe with controller, reflux condenser and a nitrogen blanket.

The reaction mixture was heated to a temperature of 125°C over a period of 50 minutes and held at that temperature for approximately 48 hours. After 48 hours, about 94.2% conversion of the methyl salicylate to alkyl methyl salicylate had occurred. The reaction mixture was cooled with stirring overnight to a temperature of about 50°C.

The crude alkyl methyl salicylate was removed from the reaction flask by using a gas dispersion tube and pulling it into a four liter flask under vacuum. The catalyst remained in the reaction flask. Product remaining on the catalyst was removed by rinsing the contents of the flask with approximately 400 ml portions of toluene while stirring, followed by pulling the toluene and crude product into a two liter flask through a gas dispersion tube under vacuum. This rinsing/pulling procedure was repeated additional three times. The toluene recovered in this procedure was stripped on a rotovap at a temperature of approximately 95°C to 100°C



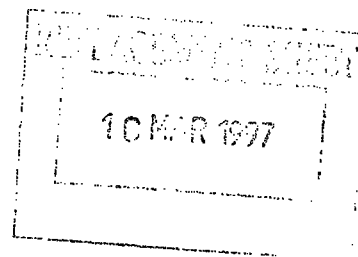
under vacuum ($\sim$ 25 mm of Hg vacuum) and the resulting stripped product was combined with the recovered crude alkylated methyl salicylate.

The combined crude alkylated methyl salicylate was then stripped at a temperature of about 130°C at a pressure of approximately 1 to 10 mm of mercury. Further stripping was conducted at a temperature of about 185°C to 191°C at a pressure of approximately 1 to 10 mm of mercury. Product analysis indicated that about 94.7 weight percent of the methyl salicylate was alkylated.

**Example 2 -- Preparation of Alkyl Methyl Salicylate Using
1:1 Molar Ratio of Olefin to Methyl
Salicylate**

Methyl salicylate commercially obtained from Aldrich Chemical Company, Milwaukee, Wisconsin, USA was alkylated using a long chain carbon feed. In this example, 617.9 grams (2.0 moles) of a C_{20} - C_{24} alpha olefin fraction (available from Chevron Chemical Company, San Ramon, California, USA), was charged to a 2 liter, three-neck oven dry flask. 304.3 grams (2 moles) of methyl salicylate, followed by 150 grams of AMBERLYST®36 (a solid acidic sulfonic acid resin catalyst commercially available from Rohm & Haas, Philadelphia, Pennsylvania, USA), were next charged to the flask. The flask was then equipped with a stirrer, temperature probe with controller, reflux condenser and a nitrogen blanket.

The reaction mixture was heated to a temperature of 135°C over a period of 25 minutes and held at that temperature for approximately 61 hours while periodically removing aliquots to check reaction completion. After 61 hours, the recovered

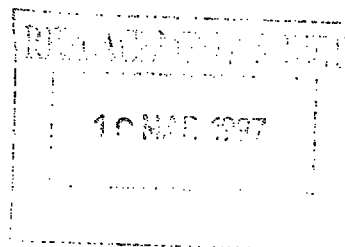


product was analyzed for its components which analysis is reported in Table I below:

TABLE I COMPONENTS IN RECOVERED ALKYLATED METHYL SALICYLATE	
COMPONENT	WEIGHT PERCENT
Salicylic acid	1.5%
Olefin	6.5%
Alkyl methyl salicylate	87.5%
Methyl salicylate	4.5%

The product was filtered through a sintered glass filter. The filtered alkyl methyl salicylate was heated to a temperature of 210°C over a period of about 45 minutes and then stripped under vacuum of about 1 to 10 mm of Hg was applied. These stripping conditions were maintained for about 30 minutes. The stripped product was next cooled to 150°C and the vacuum broken with a nitrogen stream. 739.9 grams of product was recovered. Analysis of this product is set forth in Table II below:

TABLE II COMPONENTS IN RECOVERED AND STRIPPED ALKYLATED METHYL SALICYLATE	
COMPONENT	WEIGHT PERCENT
Salicylic acid	0.1%
Olefin	4.7%
Alky methyl salicylate	95.2%



Example 3 -- Preparation of Overbased Alkyl Methyl Salicylate Additive Composition in the Absence of Carbon Dioxide

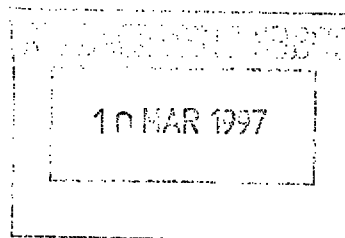
Alky methyl salicylate produced in the manner similar to either Example 1 or 2 above is overbased with an excess of calcium hydroxide. In this example, 100 grams of C₂₀-C₂₄ alkylated methyl salicylate is combined into approximately 500 ml of 2-ethylhexanol at room temperature. About 20 grams of lime are added to the solution and the solution is maintained at about 30°C for about 2 hours. Afterwards, the 2-ethylhexanol diluent is removed by stripping to provide for an overbased alkylated alkyl salicylate having a TBN of greater than zero and less than about 100.

Example 4 -- Preparation of Overbased Alkyl Methyl Salicylate Additive Composition Containing Carbon Dioxide

To a 2 liter, 4-neck round bottom flask were added 100 grams of methanol, 480 grams of xylene, and 90 grams of Mississippi Lime (Mississippi Lime Company, Ste. Genevieve, Missouri, USA). The resulting system was stirred for 10 minutes. Afterwards, 266 grams of alkyl methyl salicylate, prepared in a manner similar to that of Examples 1 and 2, was slowly added to the system, over about a 1.5 hour period, while maintaining a maximum temperature of 31°C.

At this point, carbonation was initiated and approximately 28 grams of carbon dioxide were added at the following rates:

- 17.5 grams CO₂ at 0.295 grams/minute
- 2.4 grams CO₂ at 0.224 grams/minute
- 2.8 grams CO₂ at 0.183 grams/minute
- 2.8 grams CO₂ at 0.140 grams/minute
- 2.8 grams CO₂ at 0.061 grams/minute



Upon completion of the carbonation step, the system was heated to 93°C over a 2 hour period and then heated to 132°C over a 30 minute period. At this point, 155 grams of diluent oil, CitCon 100N, was added and the system heated to 204°C over 1.5 hours under vacuum to strip of the xylene. The resulting solution was then filtered over Celite™ (diatomaceous earth available from Manville Corporation) so as to provide an overbased carbon dioxide containing alkyl methyl salicylate additive composition having a TBN of about 182 and a viscosity of 100°C of about 19 cSt.

Proton nuclear magnetic resonance spectroscopy (¹H-nmr) and infrared spectroscopy of the resulting composition indicated the retention of the methyl ester in the overbased product.

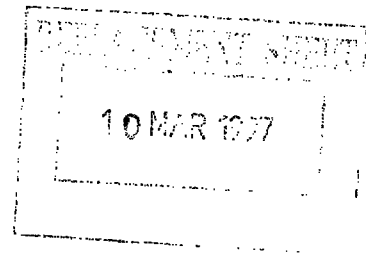
Example 5 -- Dispersion Test

Overbased Alkylated alkyl salicylate prepared in Example 4 above was tested for dispersancy in the following dispersion test. In this test, the dispersant ability of the formulated lubricating oil composition is obtained by conducting chromatography on paper of a mixture of the lubricating oil composition to be tested and an artificial sludge under the following conditions:

Spot No. 1	Ambient temperature without water
Spot No. 2	10 minutes at 200°C without water
Spot No. 3	10 minutes at 250°C without water
Spot No. 4	Ambient temperature with 1% water
Spot No. 5	10 minutes at 200°C with 1% water
Spot No. 6	10 minutes at 250°C with 1% water

The spots are rated after 48 hours. For each spot, the diameters of diffusion of soot (d) and of the oil (D) are measured and the ratio

$$\frac{d}{D} \times 100$$



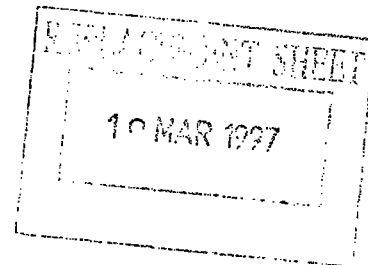
is calculated. The dispersancy of the oil over a variety of conditions is obtained from the sum of the six spot ratings. Oils having values of greater than about 250 are considered to have dispersant properties and are compared to reference oils, i.e., an oil having 23.4 weight percent of commercially available salicylate under otherwise identical parameters.

The lubricating oil composition was prepared by combining 22 weight percent of an overbased alkylated alkyl salicylate similar to that of Example 4 above, 0.67 weight percent of a zinc dithiophosphate and 1.60 weight percent of an alkenyl succinimide to a SAE 30 oil. The resulting composition has 1.505 weight percent calcium, 0.080 weight percent zinc; 0.050 weight percent phosphorus; 0.03 weight percent nitrogen; a TBN of about 40.2; and a viscosity of 100°C of 11.8 cSt.

20 grams of this test composition were then combined with 5 grams of sludge containing 2% of carbonaceous material. The mixture is then homogenized. In the samples containing water, 1% water (250 μ l) is added to the composition prior to homogenizing.

The freshly homogenized test lubricating oil composition (20 μ l of each but done in duplicate) are syringed onto 2 separate sheets of paper using a 100 μ l syringe. The heated samples are first incubated in a heating bath at the indicated temperature for 10 minutes before application.

The papers are stored in the horizontal position for 48 hours at a temperature of from about 20° to about 25°C. Storage is conducted under conditions to shelter the papers from dust.

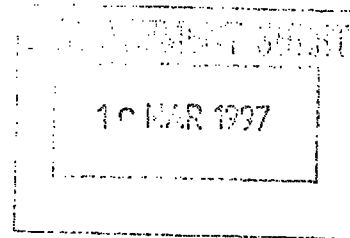


After 48 hours, the spots should be circular and the zone of dispersion of the soot (d) as well as the zone of the dispersion of the oil (D) are measured. For additives providing good dispersancy, the sum of the six values of $d/D \times 100$ should be at least 250. In the present case, the sum was 312. This indicates that the salicylates of this invention possess dispersant properties. Additionally, comparison to reference oil indicates similar properties, i.e., the sum of these 6 spots for the reference oil was 332.

Example 6 -- Hydrolytic Stability Test

Overbased alkylated alkyl salicylate prepared in Example 4 was tested for its hydrolytic stability. The test comprises preparing a formulated lubricating oil composition wherein the TBN is derived primarily from the overbased alkylated alkyl salicylate composition. In the present case, the tested lubricant compositions were formulated with 1 weight percent of a succinimide dispersant and 8 mmoles of a ZnDTP containing secondary alkyl groups in a base stock which was additionally formulated with 22 weight percent of the alkylated alkyl salicylate so as to provide for a TBN of about 40.

In this test, 98 grams of the formulated lubricating oil composition and 2 grams of distilled water are combined and sealed in a pressure type beverage bottle. The bottle is rotated end over end for about 70 hours in a convention oven maintained at about 93°C. The bottles are then cooled to room temperature and the contents thereof are poured into a centrifuge tube and spun at 10,000 rotations per minute for about 60 minutes at room temperature. The TBN of the oil layer is then determined and loss of TBN relates to the hydrolytic stability of the lubricant oil composition -- the

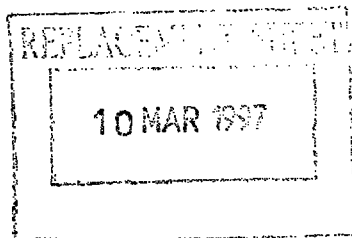


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greater the loss of TBN the less hydrolytically stable the lubricant oil composition was.

In this test, the resulting TBN loss was 3% which reflected that these compositions were hydrolytically stable. Additionally, the amount of filtered deposits was 0.09% which indicated little formation of solid residues upon exposure to water.

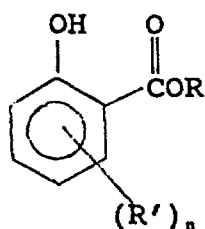
While the invention has been described in terms of various preferred embodiments, the skilled artisan will appreciate that various modifications, substitutions, omissions, and changes may be made without departing from the spirit thereof. Accordingly, it is intended that the scope of this invention be limited solely by the scope of the following claims, including equivalents thereof.



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WHAT IS CLAIMED IS:

1. A lubricating oil soluble, overbased alkylated alkyl salicylate composition wherein said composition has a TBN of from greater than 0 to about 300 and further wherein said alkylated alkyl salicylate has the formula prior to overbasing of:



wherein R is alkyl of from 1 to about 6 carbon atoms; R' is an alkyl group of from about 15 to 50 carbon atom; and n is an integer of from 1 to 2.

2. The composition according to Claim 1 wherein R is methyl and R' is an alkyl group of from about 20 to about 50 carbon atoms.
3. The composition according to Claim 1 wherein R' is a mixture of C₂₀-C₂₄ alkyl groups.
4. The composition according to Claim 1 wherein said overbased alkylated alkyl salicylate has a TBN of from greater than 0 to about 100.
5. The composition according to Claim 1 wherein said overbased alkylated alkyl salicylate has a TBN of from greater than about 100 to about 300.
6. The composition according to Claim 1 which further comprises from about 5 to 95 weight percent of a diluent oil.

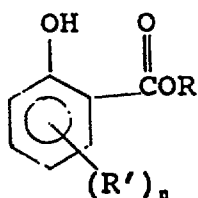
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7. A lubricating oil soluble, overbased alkylated alkyl salicylate composition which is prepared by the process which comprises:

(a) combining into a diluent from about 15 to about 50 weight percent of an alkylated alkyl salicylate based on the total weight of the alkylated alkyl salicylate/diluent composition wherein said alkylated alkyl salicylate is of the formula

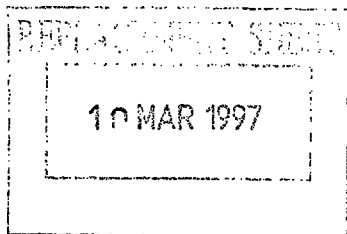


where R is alkyl of from 1 to about 6 carbon atoms; R' is an alkyl group of from about 15 to about 50 carbon atom; and n is an integer of from 1 to 2;

(b) combining a sufficient amount of an alkaline earth metal base into the composition produced in (a) above under conditions wherein the amount of alkaline earth metal is incorporated into the salicylate in excess of that necessary to neutralize the alkylated alkyl salicylate; and

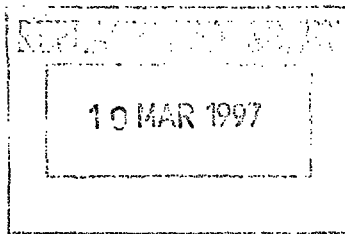
(c) optionally contacting from about 0.1 to about 1.5 molar equivalents of carbon dioxide based on each molar equivalent of alkylated alkyl salicylic acid under conditions wherein carbon dioxide is incorporated into the composition wherein the overbased composition has a TBN of from greater than 0 to about 300.

8. The composition according to Claim 7 wherein the alkaline earth metal base is selected from the group consisting of an alkaline earth metal oxide, hydroxide, and C₁ to C₆ alkoxide.



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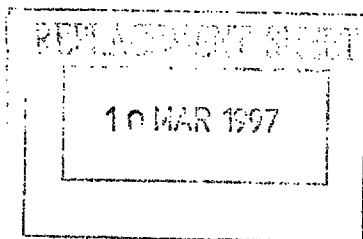
9. The composition accordingly to Claim 8 wherein the alkaline earth metal base is calcium hydroxide.
10. The composition according to Claim 7 wherein R is methyl and R' is an alkyl group of from about 20 to about 50 carbon atoms.
11. The composition according to Claim 10 wherein R' is a mixture of C₂₀-C₂₄ alkyl groups.
12. The composition according to Claim 7 wherein said overbased alkylated alkyl salicylate is prepared in the absence of carbon dioxide wherein said composition has a TBN of greater than 0 and less than 100.
13. The composition according to Claim 12 wherein said overbased alkylated alkyl salicylate has a TBN of greater than 0 and less than 50.
14. The composition according to Claim 7 wherein said overbased alkylated alkyl salicylate is prepared using carbon dioxide.
15. The composition according to Claim 7 which further comprises from about 5 to 95 weight percent of a diluent oil.
16. A lubricating oil composition comprising an oil of lubricating viscosity and from about 2 to about 30 weight percent of an overbased alkylated alkyl salicylate additive composition according to Claim 1.
17. A lubricating oil composition comprising an oil of lubricating viscosity and from about 2 to about 30



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weight percent of an overbased alkylated alkyl
salicylate additive composition according to Claim 2.

18. A lubricating oil composition comprising an oil of
lubricating viscosity and from about 2 to about 30
weight percent of an overbased alkylated alkyl
salicylate additive composition according to Claim 3.
19. A lubricating oil composition comprising an oil of
lubricating viscosity and from about 2 to about 30
weight percent of an overbased alkylated alkyl
salicylate additive composition according to Claim 4.
20. A lubricating oil composition comprising an oil of
lubricating viscosity and from about 2 to about 30
weight percent of an overbased alkylated alkyl
salicylate additive composition according to Claim 5.
21. A lubricating oil composition comprising an oil of
lubricating viscosity and from about 2 to about 30
weight percent of an overbased alkylated alkyl
salicylate additive composition according to Claim 6.
22. A lubricating oil composition comprising an oil of
lubricating viscosity and from about 2 to about 30
weight percent of an overbased alkylated alkyl
salicylate additive composition according to Claim 7.
23. A lubricating oil composition comprising an oil of
lubricating viscosity and from about 2 to about 30
weight percent of an overbased alkylated alkyl
salicylate additive composition according to Claim 8.



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24. A lubricating oil composition comprising an oil of lubricating viscosity and from about 2 to about 30 weight percent of an overbased alkylated alkyl salicylate additive composition according to Claim 9.
25. A lubricating oil composition comprising an oil of lubricating viscosity and from about 2 to about 30 weight percent of an overbased alkylated alkyl salicylate additive composition according to Claim 10.
26. A lubricating oil composition comprising an oil of lubricating viscosity and from about 2 to about 30 weight percent of an overbased alkylated alkyl salicylate additive composition according to Claim 11.
27. A lubricating oil composition comprising an oil of lubricating viscosity and from about 2 to about 30 weight percent of an overbased alkylated alkyl salicylate additive composition according to Claim 12.
28. A lubricating oil composition comprising an oil of lubricating viscosity and from about 2 to about 30 weight percent of an overbased alkylated alkyl salicylate additive composition according to Claim 13.
29. A lubricating oil composition comprising an oil of lubricating viscosity and from about 2 to about 30 weight percent of an overbased alkylated alkyl salicylate additive composition according to Claim 14.

OVERBASED ALKYLATED ALKYL SALICYLATES

ABSTRACT OF THE DISCLOSURE

This invention is directed to overbased alkyl alkyl salicylate which are useful additives for lubricating oil compositions. In particular, the compositions, of this invention impart detergency and discrepancy to the lubricating oil composition as well as provide for alkalinity reserve.

