DIALKYSALICYLIC ACIDS AND ALKALINE EARTH METAL SALTS THEREOF

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4 Claims

ABSTRACT OF THE DISCLOSURE

Alkylsalicylic acids having a high degree of para-substitution and having the alkyl group attached to the benzene nucleus by a quaternary carbon atom are prepared from tertiary alkylating agents and in particular by a two stage alkylation of phenol using a straight chain monoolefin in the first stage and a branched monoolefin in the second stage. The polyvalent metal salts of said acids are excellent lubricant and fuel additives characterized by improved high temperature performance, the ability to keep the interior of engine cylinders clean, and to counteract deposition of carbonaceous material on pistons and piston ring grooves.

BACKGROUND OF THE INVENTION

This invention, therefore, relates to alkylsalicylic acids and their polyvalent metal salts as novel compounds and to processes to prepare these compounds. The invention particularly relates to the application of basic polyvalent compounds as additives in lubricants and fuels.

British Pat. 1,146,925 relates to lubricant compositions with improved dispersant properties at high temperatures, comprising one or more lubricants and one or more salts of polyvalent metals and alkylsalicylic acids, which alkylsalicylic acids contain at least one alkyl group having more than 12 carbon atoms and of which more than 60% m. consists of acids with an alkyl group that is attached to the benzene nucleus in para-position relative to the hydroxyl group.

As possible modes of preparation for these salts the specification pertaining to the said application describes four routes starting from phenol, ortho- and para-cresol and salicylic acid. The one starting from phenol is economically the most attractive. Phenol is alkylated with cetene and the alkylphenols thus obtained are converted into the corresponding alkylsalicylic acids by phenation, carboxylation and hydrolysis. This process yields a mixture of alkylsalicylic acids of which 88% m. contains an alkyl group that is attached to the benzene nucleus in para-position relative to the hydroxyl group. These acids can be converted via conventional methods into the desired salts.

For the preparation of the salts on a large scale the use of pure cetene as alkylating agent is less attractive economically. Olefin mixtures seem to be better suited and according to examples given in the aforementioned specification, satisfactory results can be obtained with C12—C18 olefin mixtures as the alkylating agent.

Investigation has now shown that if these olefin mixtures are used for the alkylation of phenol, the alkylate thus obtained contains, besides the desired alkylation products of 4-alkylphenol and 2,4-dialkylphenol, a considerable quantity of 2-alkylphenol. If this alkylate is converted in the usual manner into a mixture of salts of polyvalent metals and alkylsalicylic acids, the mixture contains a high proportion of salts of 3-alkylsalicylic acid originating from the 2-alkylphenol. As described in the aforementioned specification, the latter salts, after incorporation in a lubricant, do not show a significant improvement in dispersant properties at high temperatures over mixtures of salts of polyvalent metals and alkylsalicylic acids already known.

Efforts to find a suitable way to decrease the quantity of 2-alkylphenol in the alkylate have hitherto failed. For example, the quantity of 2,4-dialkylphenol was increased at the cost of the quantity of 2-alkylphenol, formed during alkylation by applying more severe alkylation conditions (higher alkylating excess of olefins). However, this only led to an increase in the percentage of noncarboxylatable 2,4,6-trialkylphenol in the alkylate, while the yield of 2,4-dialkylphenol hardly increased. Another possibility investigated was the separation of the 2-alkylphenol from the mixture of alkylphenols. The salts formed by vacuum distillation and is relatively expensive, leads only to the separation of mono- and dialkylphenols, so that not only the undesired 2-alkylphenol, but also the 4-alkylphenol, which is suitable for further conversion into alkylsalicylic acid, is removed from the alkylphenol mixture.

SUMMARY OF THE INVENTION

It has now been found that in the preparation of alkylsalicylic acids by alkylation of phenol followed by phenation, carboxylation, and hydrolysis the formation of a substantial amount of 3-alkylsalicylic acid can be prevented if the alkylation is completely or partly carried out with an alkylating agent which attaches preferentially to the benzene nucleus in para-position relative to the hydroxyl group. These alkylation agents have such a structure that the alkyl group attaching to the benzene nucleus is attached to it with a quaternary carbon atom. The acids so obtained and their corresponding salts subsequently obtained are novel compounds.

The invention, therefore, relates to salts of polyvalent metals and alkylsalicylic acids containing at least one alkyl group having more than 12 carbon atoms and having an alkyl group in the para position relative to the hydroxyl group, the para positioned alkyl group being attached to the benzene nucleus by a quaternary carbon atom.

Alkylation agents having such a structure that the alkyl group which attaches to the benzene nucleus is attached to it with a quaternary carbon atom, will for the sake of brevity be indicated hereinafter as "tertiary alkylation agents." Generally at least 75% m. of the para-positions of the alkyl groups are attached to the benzene nucleus by a quaternary carbon atom.

In the preparation of the salts by the alkylation of phenol, the alkylation can be carried out in various ways. For example, phenol can be alkylated with a tertiary alkylation agent containing more than 50% m. tertiary alkyl groups in the molecule. Examples of such tertiary alkylation agents are dimers, trimers or polymers of monoolefins which are branched at one or both of the carbon atoms adjacent to the double bond, such as tetrasubutene and higher polyisobutenes, trisopentene and higher polyisopentenes, disoctenes and higher polyoctenes etc. or precursors for these olefins such as monoalkylalkyl ethers in which the hydroxyl group is attached to a tertiary carbon atom or occurs in a 2-position relative to a tertiary carbon atom in the molecule.

The alkylation of the phenol is preferably carried out in two stages using a different alkylation agent in each stage, one of which is a tertiary alkylation agent having from 4 to 12 carbon atoms in the molecule and the other an alkylation agent containing a hydrocarbon group having from 12 to 30 carbon atoms. Examples of suitable tertiary alkylation agents for this purpose are 4-alkylaromatic compounds having from 4 to 12 carbon atoms in the molecule which are branched at one or both of the carbon atoms adjacent to
the double bond, or precursors for these olefins. Very suitable are monoolefins with the general formula

$$R - \text{C} = \text{C}H_2$$

in which R represents an alkyl group having from 1 to 9 carbon atoms. Examples of such monoolefins are isobutene, isopentene and isohexene. Particularly suitable is isobutene. Examples of suitable alkylating agents which can be used in combination with the above-mentioned tertiary alkylating agents are straight-chain olefins having from 12 to 30 carbon atoms in the molecule, for example tridecene, tetradecene, pentadecene, etc. Mixtures of such straight-chain monoolefins are very suitable, in particular such olefin mixtures obtained by means of urea extraction or by selective separation by means of molecular sieves.

In general, olefins suitable for alkylolation have less than about 50 carbon atoms and preferably less than 25 carbon atoms.

Alkyl groups attached with a quaternary carbon atom to the benzene molecule, such as tertiary butyl groups, show the tendency to shift under the prevailing alkylolation conditions for example a shift from the para to the ortho position. This shift is proportionally greater the longer the alkylate is in contact with the alkylolation catalyst. Since the two-stage alkylolation of phenol has as its primary purpose a maximum yield of para-substituted material, the contact between the para-tert-alkylphenol and the alkylolation catalyst should be as short as possible. In this connection the two-stage alkylolation of phenol as hereinbefore described is preferably carried out in such a way that the tertiary alkylation agent is applied in the second stage.

Acid-activated clays have been found to be very suitable for the alkylolation of phenol and the alkylphenols. The quantity of catalyst used is as a rule 1-10% w., in particular 3-7% w. relative to the sum of the quantities by weight of the alkylolation agent and the phenol to be alkylated.

The clay catalysts can be composed of naturally occurring clays or may be synthesized. One exemplary synthesized type contains alumina in the range of 15-30% Al₅O₃, another synthesized type is produced from various kinds of clays. However, the most frequently used clay catalysts come from naturally occurring sources, such as bentonites composed of montmorillonite, from halloysites, and from kaolinite clays.

The specific type of clay used is not very critical if the clay selected is low in iron content and substantially free from various elements such as heavy metals which would favor either poisoning of the catalyst or the production of undesired products. Both pellet or “fluid” powder forms can be used. The clays are usually activated by treatment with a mineral acid, such as sulfuric, at moderately elevated temperatures.

The alkylolation of phenol with straight-chain monoolefins having from about 12 to 30 carbon atoms in the molecule is preferably carried out at temperatures between 175 and 225°C, preferably with 0.6 to 1.0 mole of olefin per mole of phenol.

The alkylolation of the alkylphenols with branched monoolefins having the general formula $R - \text{C} = \text{C}H_2$ in which R represents an alkyl group having from 1 to 9 carbon atoms, is preferably carried out at temperatures between 50 and 200°C, preferably with 1.0 to 1.5 mole of olefin per mole of alkylphenol.

The conversion of the alkylphenols thus prepared into the corresponding alkylsalicylic acids can be effected according to any of the techniques known in the art. One suitable technique is as follows:

Using an alcoholic caustic solution the alkylphenols are converted into the corresponding alkylphenolates, which are then treated with CO₂ at about 140°C. C. and a pressure of 10 to 30 atm, the alkylsalicylic acids are then obtained from the alkylsalicylates by using, for example, a 30% sulphuric acid solution.

The salts according to the invention are suitable for use as additives in lubricating oils and fuels. They are of special importance as additives in lubricating oils, because they are capable of keeping the interior of engine cylinders, in particular diesel engine cylinders, clean, and of countering deposition of carbonaceous products on pistons and in piston ring grooves.

When the salts according to the invention are used as lubricant additives, basic salts are preferable because these salts, in addition to their dispersant action, are capable of neutralizing acid compounds formed during the combustion process in the engine. A basicity up to about 250% is in most cases sufficient. Favorable results can, however, be obtained by using polyvalent metal salts of the present type with a basicity between 25 and 225%, e.g. polyvalent metal salts with a basicity of about 50% or of about 200%. Particularly eligible among the salts of polyvalent metals and alkylsalicylic acids as lubricant oils additives are the salts of bivalent metals. Preference is given to salts of Group II metals, particularly alkaline earth metals and in particular calcium salts.

Therefore, the preferred salts are the basic barium, calcium, magnesium and strontium salts.

The conversion of the alkylsalicylic acids into neutral as well as basic salts can be effected according to techniques generally known in the art, and used for such conversions. For the preparation of neutral calcium salts the alkylsalicylic acids can, for example, be converted into the corresponding sodium salts, which are then allowed to react with an equivalent quantity of CaCl₂. For the preparation of basic calcium salts with a relatively low basicity, for example 50%, one can treat the alkylsalicylic acids with two equivalents of calcium in the form of Ca(OH)₂. For the preparation of basic calcium salts with a higher basicity, for example 200%, the alkylsalicylic acids can be treated with four equivalents of calcium in the form of Ca(OH)₂ while introducing 1.6 equivalents of CO₂.

The basicity of these metal salts is usually defined as the excess of metal in the basic salts over that quantity of metal which would be present in the normal (non-basic) salts alone. Thus a mixture of 0% basicity would denote a mixture containing the metal only in the form of the normal salt and a mixture of 100% basicity would denote a mixture containing twice as many equivalents of the metal as the number of equivalents of replaceable acidic hydrogen atoms in the acid. If the content of metal in a particular mixture is (a) percent by weight, and if the content of the metal the mixture would have if it were present only as the normal salt is (b) percent by weight then the basicity of the mixture is

$$\frac{(a) - (b) \times 100}{(b)}$$

As stated hereinbefore, the metal salts preferably should be derived from alkylsalicylic acids containing at least one alkyl group with more than 12 carbon atoms. For application in lubricant oils metal salts of alkylsalicylic acids containing at least one alkyl group with at least 14 carbon atoms, such as metal salts of alkylsalicylic acids containing an alkyl group with 15-18 carbons are preferably.

With respect to the molar percentage of the acids containing an alkyl group attached to the benzene nucleus in para-position relative to the hydroxyl group, alkylsalicylic acids in which the molar percentage is from at least 60 to more than 70% m. are preferred.

The lubricating oils employed in the present invention can be mineral or synthetic. The preferred mineral oils are generally paraffinic and/or naphthenic in character. The viscosity can vary within wide limits so that the oils belonging to S.A.E. grades from 5W to 70W are acceptable. Suitable oils can also be derived from highly
paraffinic or highly naphthenic oils with substantial amounts or aromatics. Chemical or selective solvent treatment can be used if desired. Mixed base crudes and high aromatic crudes containing paraffinic hydrocarbons are also suitable base stocks after refining.

The mineral oil bases can be blends of distillate lubricating oils and bright stocks or they can be mixed with, or even entirely replaced by, synthetic lubricants or polymerized olefins such as polyisobutylene. The polyvalent salts of the invention can also be added to lubricating greases. The salts of the polyvalent metals and the alkyllsalicylic acids can be incorporated as such in the lubricant or in the form of a concentrate that has been obtained, for example, by mixing the salts with a small quantity of oil.

The concentration of the present metal salts in the lubricant can vary within wide limits. The salts are generally present in such amounts as to give an average T.B.N.E. in the range of 5–12 preferably 6–10. In general, the desired dispersancy is obtained if the lubricants contain 0.01 to 5% w., in particular 0.1 to 1% w., of polyvalent metal in the form of the instant salts of polyvalent metals and alkyllsalicylic acids.

In addition to the salts of the polyvalent metals and the alkyllsalicylic acids, the lubricant compositions may contain other additives, such as antioxidants, foam inhibitors, anti-corrosion agents, viscosity and/or viscosity index improvers, agents to improve the lubricating action and other substances which are usually added to lubricants. It is desirable to use relatively small amounts of other additives, e.g., from 0.01 to about 2% w. by weight of the composition. These examples are in no way meant to limit the number or kind of additives that may be incorporated into lubricants in addition to polyvalent metal salts. Any suitable additive desired may be incorporated.

The following series of examples show prior art methods as well as the improved method of the invention of alkylation phenol. Examples A and B are prior art methods. Examples I and II are examples according to the present invention. The C_{15}-C_{18} olefin mixtures used in Example B, I and II was a mixture of straight-chain monoolefins with 15–18 carbon atoms, in the molecule, obtained in cracking straight-chain paraffins obtained by means of urea extraction.

**EXAMPLE A**

(According to Great Britain Pat. 1,146,925)

Phenol was alkylated at 150° C. with cetene (molar ratio 1:2.5) using 5% w. of acid clay as catalyst. The alkyphenols thus obtained were converted into the corresponding alkyllsalicylic acids by phentation, carbonylation and hydrolysis. In this way 1 mol of phenol yielded 0.65 mole of alkyllsalicylic acids with the following composition:

- 12% m. of 3-cetylallicylic acid
- 88% m. para-substituted
- 12% m. of 5-cetylallicylic acid
- 76% m. of 3,5-dicytallicylic acid

**EXAMPLE B**

Phenol was alkylated at 200° C. with a mixture of C_{15}-C_{18} olefins (molar ratio 1:3.1) using 5% w. of acid clay as catalyst. The alkyphenols thus obtained were converted into the corresponding alkyllsalicylic acids by phentation, carbonylation and hydrolysis. In this way 1 mole of phenol yielded 0.50 mole of alkyllsalicylic acids with the following composition:

- 36% m. of 3-(C_{15}-C_{18}) alkyllsalicylic acid
- 64% m. para-substituted
- 16% m. of 5-(C_{15}-C_{18}) alkyllsalicylic acid
- 48% m. of 3,5-di-(C_{15}-C_{18}) alkyllsalicylic acid

**Example I**

1.3 mols of phenol, 1.0 mol of a C_{15}-C_{18} mixture of olefins and 5% w. of acid clay catalyst (relative to the sum of the quantities by weight of the alkylation agent and the phenol to be alkylated) were reacted in a first alkylation zone and were added to a glass flask provided with a stirrer, cooling coils and a gas inlet tube. The flask was heated to 190°–210° C. while stirring and bubbling nitrogen through the reactants. In a similar manner the resulting alkyphenols were then alkylated in a second zone with isobutene (molar ratio 1 to 1.1) again using 5% w. of the acid clay catalyst. The alkyl phenols obtained in the second alkylation were reacted, at room temperature and pressure, with an excess alcoholic solution of sodium hydroxide to give the corresponding alkylsodium phenates, and then pumped to the top of a steam-jacketed absorption column. The absorber operates at a temperature of 160 to 165° C. Dry CO_{2} gas was introduced into the bottom of the column. The pressure in the column was approximately 20 atmospheres. The solution from the bottom of the column, saturated with CO_{2}, was passed to a steam-jacketed reaction vessel operated at 135–145° C. The carboxylic product was acidified with a 30% sulphuric acid solution, washed and stripped of solvent. 1 mole of C_{15}-C_{18} olefins yielded 0.50 mole of alkyllsalicylic acids with the following composition:

- 5% m. of 3-(C_{15}-C_{18}) alkyllsalicylic acid
- 95% m. para-substituted
- 24% m. of 5-(C_{15}-C_{18}) alkyllsalicylic acid
- 9% m. of 3,5-di-(C_{15}-C_{18}) dialkyllsalicylic acid
- 38% m. of 3-(C_{15}-C_{18}) alkyl-5-tert. butylyllsalicylic acid
- 24% m. of 3-tert. butyl-5-(C_{15}-C_{18}) alkyllsalicylic acid

Thus, of the para-substituted acids, 40% were attached to the benzene nucleus by a quaternary carbon.

The alkyllsalicylic acids obtained were converted into calcium salts with a basicity of 50 and 200% w. by treating at about 200° C. the alkyllsalicylic acids with two and four equivalents of Ca(OH)_{2} respectively while adding 1:6 equivalents of CO_{2} to the latter. The basic calcium salts so obtained were then recovered by conventional methods.

**Example II**

Phenol was alkylated at 200° C. with a mixture of C_{15}-C_{18} olefins (molar ratio 1:3:1) with 5% w. of acid clay as catalyst. The alkyl-phenols thus obtained were subsequently alkylated at 130° C. with isobutene (molar ratio 1:1.1), again with 5% w. of acid clay as catalyst. The alkyphenols obtained in this second alkylation were converted into the corresponding alkyllsalicylic acids by phentation, carbonylation and hydrolysis. In this way 1 mole of C_{15}-C_{18} olefins yielded 0.50 mole of alkyllsalicylic acids with the following composition:

- 12% m. of 3-(C_{15}-C_{18}) alkyllsalicylic acid
- 88% m. para-substituted
- 18% m. of 5-(C_{15}-C_{18}) alkyllsalicylic acid
- 9% m. of 3,5-di-(C_{15}-C_{18}) alkyllsalicylic acid
- 33% m. of 3-(C_{15}-C_{18}) alkyl-5-tert. butylyllsalicylic acid
- 28% m. of 3-tert. butyl-5-(C_{15}-C_{18}) alkyllsalicylic acid

Thus, of the para-substituted acids, approximately 38% m. were attached to the benzene nucleus by a quaternary carbon. The alkyllsalicylic acids obtained were converted into calcium salts with a basicity of 50 and 200% w. The catalyst was prepared as in Example I and the phenols were alkylated, converted into the corresponding alkyllsalicylic acids and the basic calcium salts were prepared and recovered under conditions similar to those given in Example I.

I claim as my invention:

1. A mixture of dialkyllsalicylic acids having at least one normal alkyl group with from 15–18 carbon atoms,
and at least one tertiary butyl group with the latter group attached to the benzene nucleus through the quaternary carbon atom, at least 60% of the acid molecules having an alkyl group in the para position with respect to the hydroxyl group, and at least 25% of the para-positioned alkyl groups being tertiary butyl.

2. Alkaline earth metal salts of a mixture of dialkylsalicylic acids having at least one normal alkyl group with from 15–18 carbon atoms and at least one tertiary butyl group with the latter group attached to the benzene nucleus through the quaternary carbon atom, at least 60% of the acid molecules having an alkyl group in the para position with respect to the hydroxyl group, and at least 25% of the para-positioned alkyl groups being tertiary butyl.

3. The salts according to claim 2 wherein said salts are basic and have a basicity from 25 to 225%.

4. The salts according to claim 1 wherein the alkaline earth metal is calcium.

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