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(71) Applicant: **COSMO RESEARCH INSTITUTE**
1-1, Shibaura 1-chome,
Minato-ku
Tokyo (JP)
Applicant: **COSMO OIL COMPANY, LTD**
No. 1-1 Shibaura 1-chome
Minato-ku
Tokyo (JP)

(72) Inventor: **Ueda, Sanae, c/o Cosmo Res. Inst.**
Res. and Dev. Center,
1134-2, Gongendo
Satte-shi,
Saitama (JP)
Inventor: **Takagi, Yukio, c/o Cosmo Res. Inst.**
Res. and Dev. Center,
1134-2, Gongendo
Satte-shi,
Saitama (JP)
Inventor: **Yamaoka, Shinji, c/o Cosmo Res. Inst.**
Res. and Dev. Center,
1134-2, Gongendo
Satte-shi,
Saitama (JP)

(74) Representative: **Hansen, Bernd, Dr. Dipl.-Chem. et al**
Hoffmann, Eitle & Partner,
Patentanwälte,
Arabellastrasse 4
D-81925 München (DE)

(54) Petroleum additive and process for producing alkaline earth metal salt of an aromatic hydroxy-carboxylic acid.

(57) A petroleum additive containing an alkaline earth metal salt of an aromatic hydroxy-carboxylic acid, wherein the alkaline earth metal salt is substantially free of an alkali metal and the ratio of salicylic acid skeleton to total benzene nuclei is 0.4:1 to 0.95:1. Also, a process for producing an alkaline earth metal salt of an aromatic hydroxy-carboxylic acid involving: i) reacting an alkaline earth metal salt of a phenol with carbon dioxide; ii) reacting the resulting free phenol with an alkaline earth metal reagent in the presence of 2.0 to 15.0 mol of a dihydric alcohol per 1 mol of the alkaline earth metal reagent (when no water is added) or in the presence of 0.01 to 10.0 mol of water and 1.5 to 10.0 mol of a dihydric alcohol each per 1 mol of the alkaline earth metal reagent; and iii) repeating the reaction with carbon dioxide.

Rank Xerox (UK) Business Services
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FIELD OF THE INVENTION

The present invention relates to a petroleum additive composed of an alkaline earth metal salt of an aromatic hydroxy-carboxylic acid having a specific composition with a high base number, and a process for producing the same. In particular, the present invention is directed to obtain, on an industrial scale, an additive for lubricating oils or fuel oils, especially, a petroleum additive, which is useful as a detergent.

BACKGROUND OF THE INVENTION

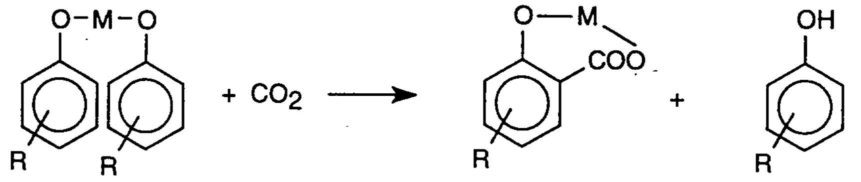
In general, an alkaline earth metal salt of an aromatic hydroxy-carboxylic acid is called an alkaline earth metal salicylate, which is used as a petroleum additive for lubricating oils for internal combustion engines or fuel oils, and which is greatly effective for neutralizing acids such as oxyacid and sulfuric acid, dispersing sludge, lacquer, and carbon, and preventing corrosive wear, ring groove plugging, and piston ring sticking, etc. In particular, due to its excellent heat stability, the alkaline earth metal salt of an aromatic hydroxy-carboxylic acid maintains the detergent activity for a relatively long period of term.

Insofar as conventional processes for producing an alkaline earth metal salt of an aromatic hydroxy-carboxylic acid are concerned, various complicated processes have been utilized. For instance, a method has been used in which an alkali metal salt of an alkylphenol is carboxylated by the Kolbe-Schmitt synthesis, the resulting alkali metal salt of an aromatic hydroxy-carboxylic acid is then neutralized with an inorganic acid, and the resulting product is further reacted with an alkaline earth metal reagent. Another method involves a metathesis using calcium chloride. Moreover, in these methods, in order to completely remove a strong acid, a strong alkali and a strong electrolyte such as chlorides (which promote corrosion of the metallic part of an engine and the like), it is indispensable to use a water washing step which thereby results in complicated processes involving a large number of steps.

Contrary to conventional knowledge in the art, the present inventors had found that the reaction of an alkaline earth metal salt of a phenol with carbon dioxide can provide an alkaline earth metal salt of an aromatic hydroxy-carboxylic acid, as disclosed in JP-B-6-717 and JP-B-4-25996. Specifically, it is a process for producing an alkaline earth metal salt of an aromatic hydroxy-carboxylic acid utilizing a simple step in which an alkylphenol (as a raw material) is reacted with an alkaline earth metal reagent to conduct a direct metal addition, then the resulting product is treated with carbon dioxide.

This process does not require the formation and decomposition of an alkali metal salt or the water washing step for removing a strong electrolyte. Thus, this process is industrially advantageous, since it can produce an alkaline earth metal salt of an aromatic hydroxy-carboxylic acid utilizing a very simple process as compared with conventional methods.

However, since this process utilizes the reaction of an alkaline earth metal salt of a phenol with carbon dioxide, free alkylphenols in an equivalent amount of an alkaline earth metal salt of an aromatic hydroxy-carboxylic acid remain in the reaction product as shown in the following reaction (I):



(I)

(where M is an alkaline earth metal and R is hydrogen, a hydrocarbon group, or a halogen atom).

The reaction product, which contains free alkylphenols in an equivalent amount of the alkaline earth metal salt of an aromatic hydroxy-carboxylic acid, provides a low base number. Furthermore, the alkylphenol is the most expensive among the raw materials and, although it can be recovered by distillation, it is exposed to a high temperature of 200 °C or more during the recovery, thereby causing a partial decarboxylation of the alkaline earth metal salt of an aromatic hydroxy-carboxylic acid.

By extensive studies, the present inventors have determined that the base number of the final product can be increased by reacting free alkylphenols formed during the production of an alkaline earth metal salt of an aromatic hydroxy-carboxylic acid with an alkaline earth metal reagent, followed by repeating a carbon dioxide treatment, while reducing the amount of the free alkylphenols. Also, the present inventors have found that a petroleum additive made of the resulting alkaline earth metal salt of the aromatic hydroxy-carboxylic acid obtained by the above process does not contain any substantial amount of an alkali metal and is considered to have a novel specific composition.

SUMMARY OF THE INVENTION

An object of the present invention is to provide a process for economically producing an alkaline earth metal salt of an aromatic hydroxy-carboxylic acid having a high base number, while avoiding decarboxylation caused by distillation at a high temperature. Furthermore, an object of the present invention is to provide a petroleum additive made of the alkaline earth metal salt of an aromatic hydroxy-carboxylic acid obtained by the above process, having a novel specific composition.

Specifically, the present invention provides:

(1) a petroleum additive made of an alkaline earth metal salt of an aromatic hydroxy-carboxylic acid, wherein the alkaline earth metal salt is substantially free of an alkali metal and the ratio of a salicylic acid skeleton to the total benzene nuclei is 0.4:1 to 0.95:1; and

(2) a process for producing an alkaline earth metal salt of an aromatic hydroxy-carboxylic acid which comprises: i) reacting an alkaline earth metal salt of a phenol with carbon dioxide; ii) reacting the resulting free phenol with an alkaline earth metal oxide or hydroxide or a mixture of both (hereinafter referred to as "an alkaline earth metal reagent") in the presence of 2.0 to 15.0 mol of a dihydric alcohol per 1 mol of the alkaline earth metal reagent (wherein no water is added) or in the presence of 0.01 to 10.0 mol of water and 1.5 to 10.0 mol of a dihydric alcohol each per 1 mol of the alkaline earth metal reagent; and iii) repeating the reaction with carbon dioxide.

DETAILED DESCRIPTION OF THE INVENTION

Production steps and operating conditions for the process for producing the alkaline earth metal salt of an aromatic hydroxy-carboxylic acid of the present invention are described below.

(a) First Carboxylation Step:

In this step, an alkaline earth metal salt of a phenol is carboxylated to obtain a hydroxy-carboxylic acid. For example, an alkaline earth metal salt of a phenol is reacted with carbon dioxide at a reaction temperature of about 150 to 240 ° C, preferably, about 160 to 230 ° C, under a reduced, atmospheric, or elevated pressure of about 5 to 10,000 KPa, preferably, about 10 to 5,000 KPa. This reaction proceeds to near completion in about 1 to 10 hours.

In the carboxylation reaction of an alkaline earth metal salt of a phenol with carbon dioxide, the presence of a large amount of water and alcohol in the reaction system decreases the carboxylation degree to yield a reduced amount of the hydroxy-carboxylic acid. Accordingly, in cases where water and alcohol are present in the reaction system, it is preferable that the reaction with carbon dioxide is conducted after removal of most, preferably all, of the water and alcohol.

(b) Metal Addition Step:

To the reaction product of the first carboxylation step, that is, the carboxylated reaction product containing free phenols, are added a dihydric alcohol, an alkaline earth metal reagent, and, if necessary or desired, a predetermined amount of water, then the mixture is reacted at a reaction temperature of generally about 60 to 200 ° C, preferably, about 90 to 190 ° C under a reduced, atmospheric, or elevated pressure of about 1 to 1,000 KPa. Prior to the second carboxylation step discussed immediately below, the water formed in this metal addition reaction and the water added for this metal addition reaction are distilled off until about 90% or more, preferably, about 99.9% or more, more preferably 100%, of the total water amount is removed, and the dihydric alcohol is distilled off until the amount of the dihydric alcohol remaining in the reaction system decreases to usually about 0.4 mol or less, preferably, about 0.3 mol or less, more preferably, about 0.2 mol or less, per 1 mol of the metal salt of the free phenol. If a large amount of the water and dihydric alcohol remains in the reaction system, the subsequent second carboxylation step results in a lowered degree of carboxylation to yield a reduced amount of the alkaline earth metal salt of a hydroxy-carboxylic acid. This metal addition reaction proceeds to near completion within a time period of about 1 to 9 hours.

(c) Second Carboxylation Step:

This step can be conducted in a manner similar to the first carboxylation step as described above. Specifically, the reaction product of the metal addition step is reacted with carbon dioxide at a reaction temperature generally of about 150 to 240 ° C, preferably, about 160 to 230 ° C under a reduced, atmospheric, or elevated pressure of about 5 to 10,000 KPa, preferably, about 10 to 5,000 KPa. This reaction proceeds to near completion within a time period of about 1 to 10 hours.

A more detailed description of the above process is set forth below.

The metal addition step and the second carboxylation step, as described above may be repeated; i.e., the conditions specified in steps (b) and (c) can be repeated.

If necessary, the unreacted phenol in the reaction product after the second carboxylation reaction may be recovered by distillation. However, the distillation or recovery may deleteriously cause decarboxylation of the reaction product to yield a reduced amount of the reaction product. Accordingly, the unreacted phenol is usually not recovered. A small amount of insoluble substances remaining in the reaction product is removed by filtration, centrifugation, etc.

Any alkaline earth metal salts of a phenol produced by any known methods can be used as the starting material. For instance, alkaline earth metal salts of a phenol may be produced by reacting phenols with an alkaline earth metal alcoholate of a C_{1-9} monohydric alcohol (e.g., methanol, ethanol, propanol, butanol) or a C_{2-6} dihydric alcohol (e.g., ethylene glycol, propylene glycol), or by reacting phenols with an alkaline earth metal oxide or hydroxide or a simple metal in the presence or absence of a monohydric or dihydric alcohol.

Phenols which can be used as the alkaline earth metal salt of a phenol include mono- or di-substituted phenols having a hydrocarbon side chain having 4 to 36 carbon atoms, preferably, 9 to 36 carbon atoms, more preferably, 12 to 32 carbon atoms, such as an alkyl group, an alkenyl group, an aralkyl group and the like. More specifically, examples of such phenols include those having a hydrocarbon group such as butyl, amyl, octyl, nonyl, dodecyl, cetyl, octadecyl, ethylhexyl, triacontyl, and the like, or a group derived from a petroleum hydrocarbon such as liquid paraffin, wax, or an olefinic polymer (e.g., polyethylene, polypropylene, polybutene). These phenols may be used either alone or as a mixture of two or more. It is desirable to use phenols which are in a liquid state at usually about 130 ° C, preferably, at about 120 ° C or lower. Exemplary phenols include butylphenol, octylphenol, nonylphenol, dodecylphenol, cetylphenol, octadecylphenol, an alkylphenol which has been alkylated with polybutene, dinonylphenol, didodecylphenol, etc.

Preferred alkaline earth metal salts of phenols include a calcium salt, a barium salt, a strontium salt or a magnesium salt of the above-mentioned phenols, with the calcium salt and the barium salt being more preferred, and with the calcium salt being especially preferred.

In the first carboxylation step (a), as mentioned above, it is possible to use the solventless method which has been applied in various salicylic acid industries. However, depending on the kind of phenols, the end use of final products, and the type of production installation, it is not problematic to use a solvent at an appropriate stage, indeed, the use of a solvent is sometimes desirable. As a solvent, almost all solvents which have been used in the Kolbe-Schmitt reaction may be used including, for example, a light aromatic hydrocarbon (e.g., toluene, xylene, ethylbenzene, cumene, diphenyl, diphenylmethane, naphthalene), a light aliphatic hydrocarbon (e.g., pentane, octane, decane, kerosine, gas oil, cyclohexane, methylcyclohexane), a ketone (e.g., methylethylketone, diethylketone, diisopropylketone, acetophenone), an ether (e.g., diphenylether, diisobutylether, dioxane, anisole), an amine (e.g., n-heptylamine, triethylamine), an amide (e.g., dimethylformamide). Also, it is possible to use phenols by themselves, as a starting material, which can be used as an alkaline earth metal salt of a phenol; further, it is possible to use a petroleum middle or heavy oil such as a lubricating oil base. For instance, in cases of producing an alkaline earth metal salt of an aromatic hydroxy-carboxylic acid for producing a lubricating oil detergent, it is possible to use a lubricating oil base which is usually used as a diluent, for instance, it is possible to co-use a lubricating oil having a viscosity of about 0.5 to 35 cSt (at 100 ° C) as a solvent for the reaction system.

The amount of free phenols in the reaction product to be produced in the first carboxylation step (a) varies depending on the carboxylation rate of the alkaline earth metal salt of a phenol, but the same equivalent amount of the alkaline earth metal salt of a phenol as a starting material can be used as a measure (in the reaction of the present invention, 1 mole of an alkaline earth metal of a phenol as a starting material in the left side in formula (I) as mentioned above is calculated as one equivalent). Accordingly, with respect to the amount of free phenols in the reaction product obtained in the first carboxylation step (a), if free phenols have been previously present in an alkaline earth metal salt of a phenol as a starting material, the amount of free phenols is the total amount of the free phenols which have been previously present and the free phenols which are produced by the carboxylation. On the basis of the total amount of these free phenols, the following metal addition step (b) is performed.

As alkaline earth metal reagents which can be used in the metal addition step (b), it is possible to use an alkaline earth metal, an alkaline earth metal alcoholate, an alkaline earth metal alkyl, and the like. For economical reasons, it is preferred to use an oxide or hydroxide or a mixture of both of an alkaline earth metal. Examples thereof include, for example, an oxide or hydroxide of calcium, barium, strontium, magnesium, etc. and a mixture thereof. The amount of the alkaline earth metal reagent to be added is preferably, 0.99 equivalent or smaller, more preferably, from 0.3 to 0.95 equivalent, per 1 equivalent of the phenol in the reaction product of the first carboxylation step (a) (i.e., the total amount of the free phenols which are formed in the reaction of an alkaline earth metal salt with carbon dioxide and the free phenols which have been previously present in an alkaline earth metal salt of an alkylphenol as a starting material).

If the amount of the alkaline earth metal reagent relative to the phenol amount is too large, the desired product having good properties cannot be obtained because the intermediate product gels and, hence, the reaction does not proceed any longer. If the amount thereof is too small, not only the product yield from the raw materials decreases, but also the recovery of the phenol is economically disadvantageous.

The dihydric alcohol to be used in the metal addition step (b) preferably has a relatively low boiling point and viscosity and is highly reactive. Preferred dihydric alcohols are those having 2 to 6 carbon atoms, with ethylene glycol, propylene glycol, and the like being especially preferred. The dihydric alcohol facilitates the reaction of the phenol with the alkaline earth metal reagent to thereby convert such into a stable oil-soluble material, and a part of the dihydric alcohol is incorporated into the final product to form an over-based salicylate. In the process according to the present invention, the metal addition reaction may be carried out either in the presence or absence of water (the presence of water is considered to be effective in enhancing the reaction).

When water is added in conducting the reaction, the dihydric alcohol is used in an amount of about 1.5 to 10.0 mol, preferably, about 1.5 to 8.0 mol, per 1 mol of the alkaline earth metal reagent to be added. When water is not added to the reaction, the dihydric alcohol is used in an amount of about 2.0 to 15.0 mol, preferably, 2.0 to 10.0 mol, per 1 mol of the alkaline earth metal reagent to be added.

If the amount of the dihydric alcohol is too small, the conversion of reaction materials, especially, the alkaline earth metal reagent to be added, into the product is lowered. If the amount thereof is too large, the removal by distillation of the excess dihydric alcohol from the reaction product requires additional time and increased utility costs, although the metal addition reaction with free phenols proceeds smoothly.

When water is added to the reaction system for the purpose of enhancing the reaction between the free phenol and the alkaline earth metal reagent in the metal addition step, any of various kinds of water can be used such as condensate water (discharged from a boiler), industrial water, and the water formed by the metal addition reaction, and the like, as well as distilled water. There is no particular limitation on water quality, and water in any state can be used such as cold water, warm water, steam, etc. The water for use in enhancing the metal addition reaction may be introduced alone to a reactor, or it may be introduced as a mixture with other reaction materials such as the dihydric alcohol and higher alcohols mentioned below. The timing of the water addition to the reactor is not particularly limited, and it may be either before or after the mixing of all reaction materials except for water. It is, however, preferred to add water within about one hour after completion of the mixing of all reaction materials. The water for use in enhancing the metal addition reaction is introduced into the reaction system in an amount of about 0.01 to 10 mol, preferably, 0.05 to 3.0 mol, per mol of the alkaline earth metal reagent to be added. When the metal addition reaction is carried out by adding water from outside into the reaction system, the reaction proceeds more smoothly and the product conversion ratio of reaction materials, especially, the alkaline earth metal reagent to be added, becomes higher, in comparison with the case when the reaction is carried out under the same conditions except that water is not added. As a result, the conversion ratio of the alkaline earth metal reagent to be added to the product decreases if the amount of water to be added to the reaction system is too small. On the contrary, if the amount of water is too large, the advantage of simplifying the distillation step after the reaction is lost.

Next, the second carboxylation step (c) is carried out. This step is substantially the same operation as in the first carboxylation step (a). Thus, no further explanation is necessary.

In the present invention, a diluent or solvent (hereinafter referred to as "diluent") having an appropriate viscosity may be added to the reaction system to facilitate the handling of the reaction materials, the intermediate products, the final products, etc. If desired, the reaction may be conducted in the presence of a diluent. In cases of producing a petroleum additive, preferred examples of the diluent include petroleum fractions having an appropriate viscosity such as paraffinic, naphthenic, and aromatic base oils and mixtures thereof. Specific examples thereof include lubricating oil fractions having boiling points of about 220 to

550 °C and viscosities of about 0.5 to 40 cSt at 100 °C. In addition thereto, organic solvents which are hydrophobic and lipophilic can be used, so long as they do not have an adverse effect on the reaction or on the use of the final product. For example, it is possible to use a higher alcohol containing 8 to 24 carbon atoms.

Although the precise structure of the reaction product obtained by the process of the present invention has not been elucidated in detail, it is considered that an alkaline earth metal salt of an aromatic hydroxy-carboxylic acid according to the present invention may be a mixture which contains a metallic salt of a salicylic acid as a main component, a metallic salt of a phenol and free phenols, since both the phenols and a large amount of the salicylic acid are detected in an oily layer obtained by hydrolyzing the reaction product and extracting the hydrolyzate with a solvent such as hexane. It is also thought that, since free phenols are formed in an equimolar amount of a metallic salt of an aromatic hydroxy-carboxylic acid from the carboxylation reaction as mentioned above, the reaction product has a chelate compound as shown in reaction (I) as mentioned above.

A petroleum additive made of an alkaline earth metal salt of an aromatic hydroxy-carboxylic acid according to the present invention can be produced by the process as mentioned above, which is substantially free of an alkali metal (5 ppm or less), and in which the ratio of the salicylic acid skeleton to the total benzene nuclei, i.e., inclusive of metal-added phenols and salicylic acids and free (unreacted) phenols and salicylic acids, is 0.4:1 to 0.95:1, preferably, 0.45:1 to 0.85:1 in the final product.

According to the process of the present invention, after carboxylation of the alkaline earth metal salt of a phenol, it is desirable to repeat the metal addition and second carboxylation reaction without recovery of free phenols by distillation (which may cause a decarboxylation), to thereby provide a final product having a high base number. In particular, this method is advantageous and economical where a long-chain alkylphenol is used as a reaction material and is difficult to be recovered by distillation. Moreover, the final product of the present invention, as produced by the process mentioned above, has a high base number, and is excellent in heat resistance.

The present invention will be further described in the following examples, but the present invention should not be construed as being limited thereto.

EXAMPLE 1

A 1-liter autoclave was equipped with a stirrer, a condenser, a nitrogen gas-introducing tube and a thermometer; and charged with 484.4 g (1.4 mol) of octadecylphenol (p-octadecylphenol content: 90.00%, o-octadecylphenol content: 9.71%), 35.47 g (0.6 mol) of 94.9%-pure calcium oxide and 168.3 g of neutral oil 150 (paraffinic lubricating oil having a viscosity of 5.27 cSt at 100 °C); and then stirred. To the resulting suspension was added a mixed solution of 50.30 g (0.81 mol) of ethylene glycol and 1.08 g (0.06 mol) of water at 130 °C under an elevated pressure of 200 KPa in a nitrogen stream. The reaction mixture was reacted at 130 °C for 3 hours under 300 KPa. While the pressure of the reaction system was gradually reduced, 11.88 g of the water (both added and produced during the reaction) and 53.83 g of a mixture of almost all of the added ethylene glycol and a small amount of octadecylphenol were distilled off to obtain 673.8 g of a liquid distillation residue having a mustard color. The temperature of the bottom residue was 184 °C and that of the distillate was 159 °C (0.3 KPa).

Carbon dioxide was then blown into 671.1 g of the distillation residue which was placed under conditions of 178 °C and 8 KPa, then elevated up to 500 KPa. The residue was allowed to stand for 4 hours to obtain 697.5 g of a liquid reaction product having a dark grayish yellow red color (designated as Reaction Product A).

Next, after the reaction system was cooled to 100 °C and the pressure was reduced to atmospheric pressure, 17.73 g (0.30 mol) of 94.9%-pure calcium oxide was added to 697.5 g of the resulting carboxylated reaction product, and then stirred. To the resulting suspension was added 93.15 g (1.5 mol) of ethylene glycol at 130 °C under an elevated pressure of 200 KPa in a nitrogen stream. The reaction mixture was then reacted at 130 °C for 3 hours under 300 KPa. While the pressure of the reaction system was gradually reduced, 4.51 g of the water produced by the reaction and 95.82 g of a mixture of almost all of the added ethylene glycol and a small amount of octadecylphenol were distilled off to obtain 708.1 g of a liquid distillation residue having a dark grayish brown color. The temperature of the bottom residue wad 185 °C and that of the distillate was 158 °C (0.3 KPa).

Carbon dioxide was then blown into 705.7 g of the distillation residue which was placed under conditions of 178 °C and 8 KPa, then elevated up to 500 KPa. The residue was allowed to stand for 4 hours to obtain 718.9 g of a liquid reaction product having a dark grayish brown color (designated as Reaction Product B).

Then, 3.54 g of an insoluble matter contained in the resulting reaction product was removed by filtration to obtain 713.6 g of a final product as a clear viscous liquid having a dark brown color. Table 1 shows the general properties of this final product and the salicylate skeleton/total benzene nuclei ratio (obtained by hydrolyzing a part of the final product, and analyzing an oily layer extracted with hexane by a liquid chromatography, then calculating the ratio based on the analyzed results; hereinafter the same).

COMPARATIVE EXAMPLE 1

In the same manner as in Example 1, 696.9 g of Reaction Product A was synthesized, and 2.64 g of an insoluble matter contained therein was removed by filtration to obtain 692.9 g of a final product as a clear viscous liquid having a dark brown color. General properties and the salicylate skeleton/total benzene nuclei ratio of this final product are shown in Table 1. From the results, it is seen that the amount of free octadecylphenol present in the final product of Comparative Example 1 is as much as about 2.1 times that in the final product of Example 1.

COMPARATIVE EXAMPLE 2

To a 1-liter three-necked pear-shaped flask was transferred 601.98 g of the final product obtained in Comparative Example 1, and subjected to reduced distillation to recover free octadecylphenols, then 73.31 g of a mixture of octadecylphenol and a lubricating oil fraction was distilled off to obtain 528.67 g of a distillation residue.

The temperature of the bottom residue was 230 ° C and that of the distillate was 217 ° C (0.3 KPa). In order to prevent decarboxylation on reduced distillation, the highest temperature of the distillation residue was adjusted to 230 ° C. In addition, the time required for distillation was about 4 hours, and the time exposed to a high temperature of 200 ° C or more was about 3 hours.

As shown in Table 1, the final product obtained in Comparative Example 1 contained 34.15% of free octadecylphenol. Thus, though 205.6 g of the recoverable free octadecylphenol should have been present, only 73.31 g of a mixture of octadecylphenol and a lubricating oil fraction was actually distilled off as mentioned above.

General properties and the salicylate skeleton/total benzene nuclei ratio of this final product are shown in Table 1. In comparison of the final product of Comparative Example 2 with that of Example 1, a carboxylic acid amount per 1 mol of calcium (COOH/Ca) is lowered, showing occurrence of decarboxylation. Since the distillation is incomplete, the free octadecylphenol amount in the final product of Comparative Example 2 is higher than that in the final product of Example 1.

EXAMPLE 2

The 1-liter autoclave used in Example 1 was charged with 393 g (1.49 mol) of dodecylphenol (p-dodecyphenol content: 93.42%, o-dodecylphenol content: 6.33%), 41.38 g (0.7 mol) of 94.9%-pure calcium oxide and 196.4 g of neutral oil 150 (paraffinic lubricating oil having a viscosity of 5.27 cSt at 100 ° C), and then stirred. To the resulting suspension was added a mixed solution of 58.68 g (0.95 mol) of ethylene glycol and 1.26 g (0.07 mol) of water at 130 ° C under an elevated pressure of 200 KPa in a nitrogen stream. The reaction mixture was reacted at 130 ° C for 3 hours under 300 KPa. While the pressure of the reaction system was gradually reduced, 10.96 g of the water (added and produced during the reaction) and 59.83 g of a mixture of almost all of the added ethylene glycol and a small amount of dodecylphenol were distilled off to obtain 619.9 g of a liquid distillation residue having a mustard color. The temperature of the bottom residue was 184 ° C and that of the distillate was 129 ° C (0.3 KPa).

Carbon dioxide was then blown into 612.9 g of the distillation residue which was placed under conditions of 178 ° C and 8 KPa, then elevated up to 500 KPa. The residue was allowed to stand for 4 hours to obtain 641.3 g of a liquid reaction product having a dark grayish yellow red color.

Next, after the reaction system was cooled to 100 ° C and the pressure was reduced to atmospheric pressure, 20.69 g (0.35 mol) of 94.9%-pure calcium oxide was added to 641.3 g of the resulting carboxylated reaction product, and then stirred. To the resulting suspension was added 108.68 g (1.75 mol) of ethylene glycol at 130 ° C under an elevated pressure of 200 KPa in a nitrogen stream. The reaction mixture was then reacted at 130 ° C for 3 hours under 300 KPa. While the pressure of the reaction system was gradually reduced, 4.11 g of the water produced by the reaction and 115.82 g of a mixture of almost all of the added ethylene glycol and a small amount of dodecylphenol were distilled off to obtain 650.7 g of a liquid distillation residue having a dark grayish brown color. The temperature of the bottom residue was

180 ° C and that of the distillate was 128 ° C (0.3 KPa).

Carbon dioxide was then blown into 648.1 g of the distillation residue which was placed under conditions of 178 ° C and 8 KPa, then elevated up to 500 KPa. The residue was allowed to stand for 4 hours to obtain 665.0 g of a liquid reaction product having a dark grayish brown color.

Then, 3.04 g of insoluble matter contained in the resulting reaction product was removed by filtration to obtain 657.8 g of the final product as a clear viscous liquid having a dark brown color. Table 1 shows the general properties of this final product and the salicylate skeleton/total benzene nuclei ratio.

COMPARATIVE EXAMPLE 3

A 500-liter autoclave was equipped with a stirrer, a condenser, a nitrogen gas-introducing tube and a thermometer, and charged with 210.4 g (0.8 mol) of dodecylphenol (p-dodecyphenol content: 93.42%, o-dodecyphenol content: 6.33%), 23.65 g (0.6 mol) of 94.9%-pure calcium oxide and 112.21 g of neutral oil 150 (paraffinic lubricating oil having a viscosity of 5.27 cSt at 100 ° C), and then stirred. To the resulting suspension was added a mixed solution of 34.08 g (0.56 mol) of ethylene glycol and 0.75 g (0.04 mol) of water at 130 ° C under an elevated pressure of 200 KPa in a nitrogen stream. The reaction mixture was then reacted at 130 ° C for 3 hours under 300 KPa. While the pressure of the reaction system was gradually reduced, 8.91 g of the water (added and produced during the reaction) and 36.36 g of a mixture of almost all of the added ethylene glycol and a small amount of dodecylphenol were distilled off to obtain 335.82 g of a liquid distillation residue having a mustard color. The temperature of the bottom residue was 193 ° C and that of the distillate was 137 ° C (0.3 KPa).

Carbon dioxide was then blown into 334.0 g of the distillation residue which was placed under conditions of 178 ° C and 8 KPa, then elevated up to 500 KPa. The residue was allowed to stand for 4 hours to obtain 351.5 g of a liquid reaction product having a dark grayish yellow red color.

Next, after the reaction system was cooled to 100 ° C and the pressure was reduced to atmospheric pressure, 16.73 g (0.30 mol) of 94.9%-pure calcium oxide was added to 351.5 g of the resulting carboxylated reaction product, and then stirred. To the resulting suspension was added a mixed solution of 17.60 g (0.28 mol) of ethylene glycol and 0.39 g (0.02 mol) of water at 130 ° C under an elevated pressure of 200 KPa in a nitrogen stream. The reaction mixture was then reacted at 130 ° C for 3 hours under 300 KPa. While the pressure of the reaction system was gradually reduced, 28.66 g of a mixed solution of almost all of the added ethylene glycol and a small amount of dodecylphenol were distilled off to obtain 357.6 g of a liquid distillation residue having a dark grayish brown color. The temperature of the bottom residue was 173 ° C and that of the distillate was 152 ° C (0.3 KPa).

Carbon dioxide was then blown into 352.6 g of the distillation residue which was placed under conditions of 178 ° C and 8 KPa, then elevated up to 500 KPa. The residue was allowed to stand for 4 hours to obtain 354.6 g of a liquid reaction product having a dark grayish brown color.

Then, 19.72 g of insoluble matter contained in the resulting reaction product was removed by filtration to obtain 329.4 g of the final product as a clear viscous liquid having a dark brown color. Table 1 shows the general properties of this final product and the salicylate skeleton/total benzene nuclei ratio.

Comparative Example 3 showed that if a dihydric alcohol amount was small in the metal addition of free phenols, the metal addition was satisfactorily conducted, whereby the amount of the insoluble matter was greatly increased and the carboxylation rate was decreased, as compared to the final product of Example 2.

TABLE 1

〈Properties of Final Products〉	Ex.1	Comp. Ex.1	Comp. Ex.2	Ex.2	Comp. Ex.3
Calcium (1) (wt%)	4.82	3.30	3.76	6.29	5.76
Base number (mgKOH/g)	135	92	105	176	161
Acid number* (mgKOH/g)	52	35	27	66	49
COOH/Ca*1 (2) (mol/mol)	0.770	0.761	0.514	0.75	0.609
Free phenol (3) (wt%)	16.06	34.15	20.03	4.73	6.69
Total benzene nuclei (4) (wt%)	67.21	69.43	68.24	56.16	59.10
Free phenol/Total benzene nuclei(mol/mol)	0.239	0.492	0.294	0.084	0.113
Insoluble matter*2 (wt%)	0.49	0.38	-	0.46	5.56
Salicylic acid skeleton/Total benzene nuclei*3	0.48	0.31	0.25	0.55	0.39

Notes:
*1: (Acid number/Base number)x2
*2: The ratio of Insoluble matter in Intermediate product before removal of Insoluble matter
*3: ((1)/Mca)x(2)/((4)/Mp)
Mca: Atomic weight of Calcium = 40
Mp: Molecular weight of Phenol
*: Acid number of Hydrolyzate

As shown in the properties of the final products set forth in Table 1, the final products obtained in Examples 1 and 2 had lower free phenol contents as compared to those obtained in Comparative Examples 1 and 2, thereby showing a higher conversion of used phenols to an aromatic hydroxyl-carboxylic acid metal salt. As compared to the final product obtained in Comparative Example 3, Examples 1 and 2 produced less insoluble matter (the insoluble matter being caused by the unreacted product of the alkaline earth metal reagent).

REFERENCE EXAMPLE 1

A hot tube test (lacquer test) was conducted in accordance with the method of Komatsu Setsubi K.K.

Samples shown in Table 2 below were diluted with neutral oil 500 (paraffinic lubricating oil having a viscosity of 10.96 cSt at 100 ° C) to make a base number of 10 mgKOH/g. The resulting samples were measured (a testing time: 16 hours, a lacquer evaluation point: 1 to 10). The higher the lacquer evaluation point, the better the heat resistance.

TABLE 2

〈Test Results〉		
	310 °C	320 °C
Example 1:	7.5	7.0
Example 2:	7.0	6.0
Product 1: (a commercially available product: AC-60C by Shell Chemical Co.)	6.5	1.0
〈Alkaline metal Concentration〉		
	Na (ppm)	K (ppm)
Example 1:	Not Detected*	Not Detected*
Example 2:	Not Detected*	Not Detected*
Product 1:	46	5
Product 2: (a commercially available product: OSCA-401 by OSCA Chemical, JAPAN)	42	550

*: not higher than 1 ppm

While the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one skill in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

Claims

1. A petroleum additive comprising an alkaline earth metal salt of an aromatic hydroxy-carboxylic acid, wherein the alkaline earth metal salt of an aromatic hydroxy-carboxylic acid is substantially free of an alkali metal and has a ratio of salicylic acid skeleton to total benzene nuclei of 0.4:1 to 0.95:1.

2. The petroleum additive as claimed in claim 1, wherein said ratio of salicylic acid skeleton to total benzene nuclei is 0.45:1 to 0.85:1.

3. A process for producing an alkaline earth metal salt of an aromatic hydroxy-carboxylic acid which comprises: i) reacting an alkaline earth metal salt of a phenol after removal of most of the water and alcohol with carbon dioxide; ii) reacting the resulting free phenol with an alkaline earth metal reagent, which is an alkaline earth metal oxide or hydroxide or a mixture of both, in the presence of 2.0 to 15.0 mol of a dihydric alcohol per 1 mol of the alkaline earth metal reagent; and iii) reacting the resulting product of step ii) after removal of most of the water and alcohol with carbon dioxide; wherein water is not added to said reaction between said free phenol and said alkaline earth metal reagent.

4. The process for producing an alkaline earth metal salt of an aromatic hydroxy-carboxylic acid as claimed in claim 3, wherein said phenols contain a hydrocarbon side chain having 4 to 36 carbon atoms.

5. The process for producing an alkaline earth metal salt of an aromatic hydroxy-carboxylic acid as claimed in claim 3, wherein said alkaline earth metal salt of a phenol is a calcium salt, a barium salt, a strontium salt or a magnesium salt of phenols.

6. The process for producing an alkaline earth metal salt of an aromatic hydroxy-carboxylic acid as claimed in claim 3, wherein said alkaline earth metal reagent is an oxide or hydroxide of calcium, barium, strontium and magnesium or a mixture thereof, and said alkaline earth metal reagent is used in an amount of 0.99 equivalent or smaller per 1 equivalent of the phenol obtained in the reaction of step i).

7. The process for producing an alkaline earth metal salt of an aromatic hydroxy-carboxylic acid as claimed in claim 3, wherein said dihydric alcohol is ethylene glycol or propylene glycol.

8. The process for producing an alkaline earth metal salt of an aromatic hydroxy-carboxylic acid as claimed in claim 3, wherein said alkaline earth metal reagent is added in an amount of ≦ 0.99 equivalent per 1 equivalent of the free phenols in the reaction product obtained in step i).

9. The process for producing an alkaline earth metal salt of an aromatic hydroxy-carboxylic acid as claimed in claim 3, wherein said steps ii) and iii) are repeated.

10. The process for producing an alkaline earth metal salt of an aromatic hydroxy-carboxylic acid as claimed in claim 3, wherein said dihydric alcohol is present in an amount of 2.0 to 10.0 mol per 1 mol of the alkaline earth metal reagent.

11. A process for producing an alkaline earth metal salt of an aromatic hydroxy-carboxylic acid which comprises: i) reacting an alkaline earth metal salt of a phenol after removal of most of the water and alcohol with carbon dioxide; ii) reacting the resulting free phenol with an alkaline earth metal reagent, which is an alkaline earth metal oxide or hydroxide or a mixture off both, in the presence of 0.01 to 10.0 mol of water and 1.5 to 10.0 mol of a dihydric alcohol earth per 1 mol of the alkaline earth metal reagent; and iii) reacting the resulting product of step ii) after removal of most of the water and alcohol with carbon dioxide.

12. The process for producing an alkaline earth metal salt of an aromatic hydroxy-carboxylic acid as claimed in claim 11, wherein said phenols contain a hydrocarbon side chain having 4 to 36 carbon atoms.

13. The process for producing an alkaline earth metal salt of an aromatic hydroxy-carboxylic acid as claimed in claim 11, wherein said alkaline earth metal salt of a phenol is a calcium salt, a barium salt, a strontium salt or a magnesium salt of phenols.

14. The process for producing an alkaline earth metal salt of an aromatic hydroxy-carboxylic acid as claimed in claim 11, wherein said alkaline earth metal reagent is an oxide or hydroxide of calcium, barium, strontium and magnesium or a mixture thereof, and said alkaline earth metal reagent is used in an amount of 0.99 equivalent or smaller per 1 equivalent of the phenol obtained in the reaction of step i).

15. The process for producing an alkaline earth metal salt of an aromatic hydroxy-carboxylic acid as claimed in claim 11, wherein said dihydric alcohol is ethylene glycol or propylene glycol.

16. The process for producing an alkaline earth metal salt of an aromatic hydroxy-carboxylic acid as claimed in claim 11, wherein said alkaline earth metal reagent is added in an amount of ≦ 0.99 equivalent per 1 mol of the free phenols in the reaction product obtained in step i).

17. The process for producing an alkaline earth metal salt of an aromatic hydroxy-carboxylic acid as claimed in claim 11, wherein said steps ii) and iii) are repeated.

18. The process for producing an alkaline earth metal salt of an aromatic hydroxy-carboxylic acid as claimed in claim 11, wherein said dihydric alcohol is present in an amount of 1.5 to 8.0 mol per 1 mol of the alkaline earth metal reagent.