

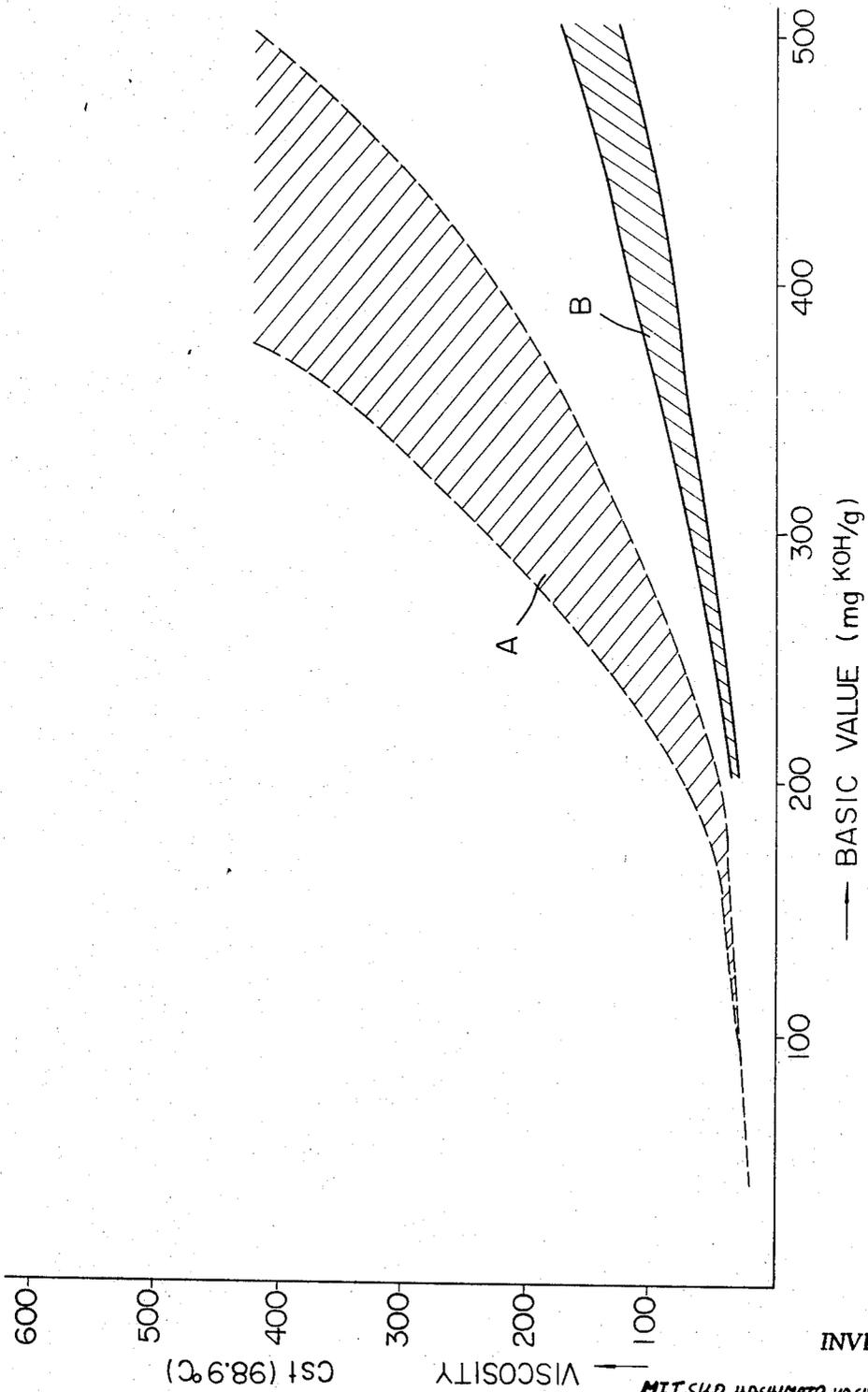
Oct. 20, 1970

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3,535,242

PROCESS FOR PRODUCING LUBRICANT ADDITIVES

Filed Sept. 25, 1967



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3,535,242

## PROCESS FOR PRODUCING LUBRICANT ADDITIVES

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Filed Sept. 25, 1967, Ser. No. 670,174

Claims priority, application Japan, Oct. 1, 1966,

41/64,470; Jan. 13, 1967, 42/2,137

Int. Cl. C01m 1/40

U.S. Cl. 252—33

4 Claims

### ABSTRACT OF THE DISCLOSURE

Process for producing an additive for a lubricant which comprises reacting a mixture of an oil solution of an oil soluble polyvalent metal salt of organic acid and a hydroxide or oxide of alkaline earth metal or magnesium with carbon dioxide in a solvent of monohydric alcohol having not less than 3 carbon atoms or petroleum solvent or a mixed solvent of the alcohol and petroleum solvent in the presence of at least one of dihydric alcohols, aminoalcohols and diamines as a reaction promoter while removing water formed in the reaction continuously from the reaction system, and repeating the carbonation treatment, if required.

### BACKGROUND OF THE INVENTION

#### Field of the invention

This invention relates to a process for producing lubricant additives having high ability of acid neutralization by treating a mixture of an oil solution of an oil soluble polyvalent metal salt of organic acid and an inorganic compound with carbon dioxide to dissolve a large amount of the inorganic compound into the oil in an oil soluble form.

#### Description of the prior art

In internal combustion engines, particularly the marine diesel engines, quite substantial wear and damage of piston rings and cylinder liners thereof are caused mainly by sulfuric acid formed at the time of combustion due to the use of low grade fuel oil containing a large amount of sulfur. The use of lubricant having a high ability of neutralizing the sulfuric acid is required to prevent such wear and damage mentioned above in the internal combustion engines. In order to satisfy the requirement, in general, organic metal salts such as overbasic metal sulfonates have been used as additives for lubricant for internal combustion engines heretofore.

In recent years, as the vessels are becoming larger in size and faster in the cruising speed, the marine engine of higher power are developed and simultaneously there is a prevailing tendency to use fuel oil of lower grade to cut down the fuel cost. Thus, the cylinder lubricants having higher ability of acid neutralization than those known heretofore are used and, as a result, the requirement for the production of additives having higher basic value than those of additives heretofore used for lubricants has been urged.

In the past, the overbasic metal sulfonates used as additives for lubricant have been produced by reacting gaseous carbon dioxide with alkaline metal hydroxides or oxides in the presence of a reaction promoter. This reaction may be referred to as "carbonation treatment" hereinafter. It has been found that when the carbonation treatment is carried out in the coexistence of water, there is inevitably imposed a limitation on the basic value of the

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product due to the turbidity of the reaction mixture and a difficulty in the filtration in the course of the process.

### SUMMARY OF THE INVENTION

It is, accordingly, an object of this invention to provide a process for producing additives for lubricant having a high basic value which may not be attained by the prior art processes known heretofore.

Another object of this invention resides in the provision of a process for producing additives for lubricant without being accompanied by the drawbacks of the prior art processes such as the turbidity and the difficulty in the filtration mentioned above.

We have found that these objects can now be accomplished by conducting the carbonation treatment while removing water formed in the course of the carbonation treatment continuously from the reaction system. In accordance with this invention, a reaction product having a basic value as high as about 300 mg. KOH/g. may be easily obtained. The basic values referred to herein were measured according to the potentiometric titration method described in JIS K2502.

In the process of this invention, any method may be readily applicable to remove water formed in the course of the carbonation treatment continuously from the reaction system so long as it permits the removal of the water under the refluxing of the solvent. Particularly, it is preferable to use a solvent which may form an azeotropic mixture with water and may be easily separated from water.

By removing water formed in the reaction continuously from the reaction system, the side-reactions wherein the reaction promoter is allowed to react mainly with inorganic salts to form materials which cause the turbidity and the difficulty in the filtration can be successfully prevented. As a result, according to the process of this invention, there can be easily obtained overbasic organic acid salts having higher basic value by using a smaller amount of the reaction promoter as compared with the prior art processes known heretofore.

In addition, if required, a product having a basic value higher than 300 mg. KOH/g., e.g. 500 mg. KOH/g., can be easily obtained in the process of this invention by repeating the carbonation treatment mentioned above twice or more times.

Although the process of this invention enables the production of additives for lubricant having high basic value, there is a disadvantage in that a slight variation in the reaction conditions leads to a considerable variance in the viscosity of the product and to a quality degradation in the lapse of time, which, in turn, present a great problem from the standpoint of quality control in the commercial production.

The reason for the variance in the viscosity and the quality degradation is that the gelation of the product is caused by the absorption of moisture in the air and this tendency becomes more prevailing as the basic value of the product becomes higher.

Such inconveniences as mentioned above can be overcome by subjecting the product to a heat-treatment in the presence of water, which may be referred to as "water-heat treatment" hereinafter, and there may be obtained a product having a uniform viscosity in a stable manner.

The mechanism of the disappearance of the gelation and the quality degradation by the water-heat treatment has not been thoroughly understood. However, it is presumed that the water-heat treatment puts the molecular arrangement of the oil soluble inorganic material in a good regularity and it is no longer susceptible to the adverse effect of the moisture in the air.

The effect of the water-heat treatment can be clearly

noted from the measuring of the viscosity and the interfacial tension of the product as well.

The process of this invention may be carried out by suspending at least one mol of hydroxide or oxide of alkaline earth metal or magnesium in an oil solution of an oil soluble alkaline earth metal salts or magnesium salt of organic acid per mol of the organic acid, adding to the resulting suspension a monohydric alcohol having not less than 3 carbon atoms or a petroleum solvent or a mixed solvent of the alcohol and petroleum solvent and blowing gaseous carbon dioxide into the resulting mixture at a boiling point of the solvent used or an azeotropic point with water in the presence of at least one of dihydric alcohols such as ethylene glycol, propylene glycol, butylene glycol, amylene glycol and pentene glycol; amino-alcohols such as ethanolamine, propanolamine, butanolamine and pentanolamine; and diamines such as ethylenediamine, propylenediamine, butylenediamine, amylenediamine and pentenediamine as a reaction promoter. In the carbonation treatment, water formed in the reaction may be removed continuously under refluxing of the solvent, or, it also may be removed from the reaction system together with the solvent. After the completion of the reaction, the solvent and the reaction promoter are distilled off and the unreacted inorganic compound is removed. Alternatively, the unreacted inorganic compound may be removed immediately after the completion of the carbonation treatment, and then, the solvent and the reaction promoter may be distilled off.

There is obtained a product having a basic value of about 300 mg. KOH/g. very easily by the single step carbonation treatment explained above, and if a product of higher basic value is required, it is convenient to adopt a multi-step process in which the product of the single step process is repeatedly subjected to the carbonation treatment after adding the reaction promoter, inorganic material and solvent thereto. As an alternative in the multi-step process, to the reaction mixture obtained by blowing gaseous carbon dioxide at a first step is replenished freshly only the inorganic material, and after repeating the operations of the carbonation by blowing carbon dioxide, the solvent and the reaction promoter are distilled off, and then, the unreacted inorganic material may be removed thereafter.

In practicing the water-heat treatment according to the process of this invention, the reaction product obtained in the above-mentioned processes is heated in the presence of water, preferably, of 3-15% by weight while raising the temperature with stirring and, then, water is removed by heating up to a temperature of 150-200° C. After treating preferably at 110-150° C. for 10-60 minutes, the temperature is then raised up to 150-200° C. to make the product substantially anhydrous.

Alternatively, after the completion of the carbonation treatment, the unreacted inorganic material is removed, the solvent and the reaction promoter are removed, then the remaining residue is heated in the presence of water of 3-15% by weight while raising the temperature with stirring and then, the water may be removed therefrom by heating up to 150-200° C.

In order to obtain a product having a basic value of higher than 300 mg. KOH/g., the above-mentioned multi-step carbonation treatment may be carried out repeatedly followed by the water-heat treatment and there can be obtained quite easily a product having a basic value of about 500 mg. KOH/g.

In the process of this invention, an amount of promoter used is preferably less than 2 mols per mol of acid group of organic acid salts. Use of more than 2 mols of promoter is less preferable because it does not produce the corresponding effects and excess amount of promoter may react with inorganic material to form a complex which causes difficulty in filtration of the product. As noted above, an amount of promoter used in this invention does not depend upon an amount of inorganic material used

but upon an amount of organic acid. A feature of this invention resides in that about equimolar amount of promoter based on the amount of organic acid is sufficient even in the process of this invention in which a large amount of inorganic material is used in order to obtain a product having a very high basic value.

The materials which may be used in the process of this invention are given in the following:

#### Organic acid salts

Organic acid salts referred to herein designate oil soluble salts of sulfonic acid, carboxylic acid and alkylphenol, and sulfonates which may be used in the process of this invention includes synthetic sulfonate, Mahogany sulfonate and the like.

Mahogany sulfonated mentioned above may be obtained by treating a lubricant fraction of petroleum with concentrated sulfuric acid or oleum to remove acid sludge therefrom, converting the resulting sulfonic acid to the form of sodium salt, extracting the resulting sodium sulfonate with an aqueous alcohol, and then, converting the same to an alkaline earth metal salt, or, by converting the sulfonic acid directly into an alkaline earth metal salt.

Synthetic sulfonate may be obtained by synthesizing an alkyl aromatic compound, sulfonating the same to sulfonic acid and converting the sulfonic acid directly to an alkaline earth metal salt.

In either of these sulfonates mentioned above, the hydrocarbon portion thereof is required to have an average molecular weight of about 350-1000 to afford the desired solubility in oil. The average molecular weight referred to herein is determined according to ASTM D-855 and the determination of the sulfonic acid is carried out by Epton method.

#### Solvents

Solvents which may be used in the process of this invention are monohydric alcohols having not less than 3 carbon atoms of petroleum solvents. These solvents serve to lower the viscosity of the reaction system to facilitate not only the agitation as well as the homogeneous reaction but also the removal of water formed in the carbonation treatment from the reaction system. When the solvent forms an azeotropic mixture with water, the removal of water can be made easier.

Although no particular restriction is imposed on the amount of solvent used, in general, an amount of more than 25% by volume, particularly 50-100% by volume based on the volume of the starting solution of organic acid metal salt in oil is preferable from the economical standpoint.

#### Inorganic compounds

Inorganic compounds which may be used in the process of this invention include hydroxides or oxides of alkaline earth metals or magnesium, and the amount used is dependent upon the basic value of the product contemplated. However, in general, more than one mol of inorganic compound per mol of sulfonic acid is required in order to obtain a product having a high basic value.

#### Reaction promoters

Reaction promoters which may be used in the process of this invention include dihydric alcohols such as ethylene glycol, propylene glycol, butylene glycol, pentene glycol, hexane glycol and heptane glycols; amino-alcohols such as aminoethanol, aminopropanol, aminobutanol and aminopentanol; and diamines such as ethylenediamine, propylenediamine, butylenediamine, pentenediamine, hexenediamine and heptenediamines. Among these exemplified above, ethylene glycol, monethanolamine and ethylenediamine have the highest activity as the reaction promoter.

Another advantage of the water-heat treatment according to the process of this invention is that the quality of the product can be greatly enhanced by such treatment.

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In general, the additives having high basic value, i.e. high ability of acid neutralization are used for lubricant for marine diesel engines. However, the oil incorporated with such additives having high basic value tends to form an emulsion with water. Since wet centrifugal purification of marine engine oils is commonly used, an excellent water separation is required for lubricant incorporated with additives, especially when it is used as a system lubricant for the marine engines. In addition, the lubricant for marine engines involves the problem of formation of rust due to the intermixing of sea water therewith, thus, the rust-preventing ability of the lubricant against saline water is an important property to be taken into account.

The lubricant incorporated with additives obtained by applying the water-heat treatment according to the process of this invention shows remarkable improvements not only in the separability from water but also in the rust-preventing ability as compared with those of untreated lubricants.

An example of the effect of the water-heat treatment in the process of this invention using various calcium sulfonates as the starting material is diagrammatically illustrated in the accompanying drawing as FIG. 1.

In FIG. 1, (A) shows the property of untreated additives and (B) shows that of water-heat treated additives.

The viscosity of the product additive is dependent upon the viscosity of the solution of the starting calcium sulfonate in oil, i.e. if the viscosity of the starting material is low, the viscosity of the product is correspondingly low, and this general tendency prevails regardless of the types of the starting material.

As can be noted from the FIG. 1, the product with the water-heat treatment shows lower viscosity and less variance than those of product without the water-heat treatment. The viscosities of the products with the treatment are lowered and the variances are minimized. FIG. 1 also shows that the higher the basic value of the additives becomes, the more remarkable the effect becomes.

#### DESCRIPTION OF THE PREFERRED EMBODIMENT

This invention will be explained more fully and practically in the following examples. It should not be construed, however, that these examples restrict this invention as they are given merely by way of illustration:

##### Comparative example

To a 300 cc. capacity four-necked flask charged with 100 g. of an oil solution of calcium petroleum sulfonate having sulfonate concentration of 0.066 mol percent, a molecular weight of 560, calcium content of 2.3% by weight and a basic value of 16.4 mg. KOH/g. were charged 30 g. of calcium hydroxide, 5 g. of ethylene glycol and 50 g. of n-butanol and the carbonation treatment was conducted with agitation under reflux of n-butanol without eliminating any water formed in the course of reaction.

After the absorption of gaseous carbon dioxide in the reaction system ceased, the temperature was raised up to 160° C. under atmospheric pressure to remove n-butanol therefrom, then, ethylene glycol was distilled off at 190° C. under a reduced pressure of 10 mm. Hg for one hour and the remaining residue was filtered by using a filter aid. The filtering was difficult and the product thus obtained was turbid. The properties of the product which was obtained in an extremely low yield were as follows:

Calcium content (wt. percent) .....	11.0
Basic value (mg. KOH/g.) .....	271
Viscosity (cst. at 98.9° C.) .....	253

As shown above, the product was extremely viscous and the yield was quite low.

##### EXAMPLE 1

To a 300 cc. four-necked flask charged with 100 g. of

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the same oil solution of calcium petroleum sulfonate as used in comparative example were charged 30 g. of calcium hydroxide, 5 g. of ethylene glycol and 50 g. of n-butanol, and to the resulting mixture was blown gaseous carbon dioxide with agitation at 117° C. under refluxing using a special refluxing tube for removing water, and water formed in the reaction was removed continuously through the refluxing tube.

After the absorption of gaseous carbon dioxide ceased, n-butanol and ethylene glycol were distilled off according to the same procedures as in comparative example and the remaining residue was filtered by using a filter aid to yield a product having the following properties. The product was clear, free from turbidity.

Calcium content (wt. percent) .....	11.9
Basic value (mg. KOH/g.) .....	300.2
Viscosity (cst. at 98.9° C.) .....	114

As can be noted from the above, the basic value of the product thus obtained is higher than that of the comparative example, the viscosity is as low as less than a half of the product of the comparative example and the product is clear, free from any turbidity.

##### EXAMPLE 2

In 100 g. of the same oil solution of an oil soluble calcium sulfonate as used in Example 1 was suspended 30 g. of calcium hydroxide and to the resulting suspension were added 2 g. of ethylene glycol and 70 g. of sec-butyl alcohol, and the resulting mixture was heated up to 100° C. with stirring and the reaction was conducted by blowing gaseous carbon dioxide thereinto.

Thereafter, the solvent, the reaction promoter and the unreacted inorganic material were removed according to the same procedures as in Example 1 to yield a product.

The product was clear and had the following properties:

Calcium content (wt. percent) .....	11.3
Basic value (mg. KOH/g.) .....	277

In contrast, the product obtained by the refluxing method in which water formed in the reaction was not removed was turbid and the basic value was 168 mg. KOH/g.

##### EXAMPLE 3

In the same oil solution of an oil soluble calcium sulfonate as used in Example 1 was suspended 30 g. of calcium hydroxide and to the resulting suspension were added 3 g. of ethylenediamine and 70 g. of iso-amylalcohol, and the resulting mixture was heated up to 120° C. with stirring and treated with gaseous carbon dioxide.

Thereafter, the solvent, the reaction promoter and the unreacted inorganic material were removed according to the same procedures as in Example 1 to yield a product. The properties of the product are as follows:

Calcium content (wt. percent) .....	12.0
Basic value (mg. KOH/g.) .....	310

In contrast, it was impossible to filter off the product in the refluxing method in which water formed in the reaction was not removed.

##### EXAMPLE 4

In 100 g. of the same oil solution of an oil soluble calcium sulfonate as used in Example 1 was suspended 30 g. of calcium hydroxide, and to the resulting suspension were added 5 g. of monoethanolamine and 50 g. of n-butyl alcohol, and the resulting mixture was heated up to 117° C. and treated with gaseous carbon dioxide thereinto. Thereafter, the solvent, the reaction promoter and the unreacted inorganic material were removed according to the same procedures as in Example 1 to yield a

product. The product was clear and had the following properties:

Calcium content (wt. percent) ----- 11.3  
Basic value (mg. KOH/g.) ----- 304

In contrast, it was impossible to filter off the product in the refluxing method in which water formed in the reaction was not removed.

#### EXAMPLE 5

In 100 g. of an oil solution of an oil soluble barium sulfonate having barium content of 7.5% by weight and a basic value of 29.5 mg. KOH/g. was suspended 30 g. of calcium hydroxide and to the resulting suspension were added 5 g. of ethylene glycol and 70 g. of n-butyl alcohol, and the resulting mixture was heated up to 117° C. with stirring and treated with gaseous carbon dioxide.

Thereafter, the solvent, the reaction promoter and the unreacted inorganic material were removed according to the same procedures as in Example 1 to yield a product.

The product was clear and had the following properties:

Barium content (wt. percent) ----- 6.8  
Calcium content (wt. percent) ----- 9.9  
Basic value (mg. KOH/g.) ----- 321.5

In contrast, it was impossible to filter off the product in the refluxing method in which water formed in the reaction was not removed.

#### EXAMPLE 6

In 100 g. of the same oil solution of an oil soluble calcium sulfonate as used in Example 1 was suspended 25 g. of calcium hydroxide, and to the resulting suspension were added 7 g. of ethylene glycol and 70 g. of mixed xylene, and the resulting mixture was heated up to 130° C. with stirring and treated with gaseous carbon dioxide.

Thereafter, the solvent, the reaction promoter and the unreacted inorganic material were removed according to the same procedures as in Example 1 to yield a product. The product had the following properties:

Calcium content (wt. percent) ----- 11.1  
Basic value (mg. KOH/g.) ----- 272

In contrast, it was impossible to filter off the product in the refluxing method in which water formed in the reaction was not removed.

#### EXAMPLE 7

In 100 g. of the same oil solution of an oil soluble calcium sulfonate as used in Example 1 was suspended 30 g. of calcium hydroxide, and to the resulting suspension were added 5 g. of a mixture of ethylene glycol and ethylenediamine in a weight ratio of 1:1, and 50 g. of n-butylalcohol, and the resulting mixture was heated up to 117° C. with stirring and treated with gaseous carbon dioxide.

Thereafter, the solvent, the reaction promoter and the unreacted inorganic material were removed according to the same procedures as in Example 1 to yield a product. The product was clear and had the following properties:

Calcium content (wt. percent) ----- 11.9  
Basic value (mg. KOH/g.) ----- 294

In contrast, it was impossible to filter off the product in the refluxing method in which water formed in the reaction was not removed.

#### EXAMPLE 8

To a 300 cc. capacity four-necked flask charged with 100 g. of an oil solution of calcium petroleum sulfonate having a sulfonate concentration of 0.004 mol %, a molecular weight of 498 and a basic value of 1.3 (mg. KOH/g.) were added 3 g. of calcium hydroxide, 5 g. of ethylene glycol and 50 g. of n-butanol, and the resulting mixture was heated up to 117° C. and treated with gaseous carbon dioxide.

Thereafter, the solvent, the reaction promoter and the unreacted inorganic material were removed according to the same procedures as in Example 1 to yield a product. The product was clear and had the following properties:

5 Calcium content (wt. percent) ----- 1.1  
Basic value (mg. KOH/g.) ----- 203

In contrast, in the refluxing method in which water formed in the reaction was not removed, the product was slightly turbid.

#### EXAMPLE 9

In 100 g. of the same oil solution of an oil soluble calcium sulfonate as used in Example 1 was suspended 30 g. of calcium hydroxide, and to the resulting suspension were added 1 g. of ethylene glycol and 80 g. of n-butanol, and the resulting mixture was heated up to 117° C. with stirring and treated with gaseous carbon dioxide.

Therefore, the solvent, the reaction promoter and the unreacted inorganic material were removed according to the same procedures as in Example 1 to yield a product. The product was clear and had the following properties:

Calcium content (wt. percent) ----- 6.95  
Basic value (mg. KOH/g.) ----- 167

25 In contrast, in the refluxing method in which water formed in the reaction was not removed, the product was slightly turbid.

#### EXAMPLE 10

30 To 100 g. of the product obtained in Example 1 were added 15 g. of calcium hydroxide, 6 g. of ethylene glycol and 50 g. of n-butanol, and the resulting mixture was heated with stirring and treated under the same conditions as in Example 1. After the absorption of gaseous carbon dioxide ceased, there was added freshly 15 g. of calcium hydroxide and the resulting mixture was treated by blowing gaseous carbon dioxide thereinto.

Thereafter, the solvent, the reaction promoter and the unreacted inorganic material were removed according to the same procedures as in Example 1 to yield a product. The product was clear and had the following properties:

40 Calcium content (wt. percent) ----- 17.9  
Basic value (mg. KOH/g.) ----- 503

In contrast, it was impossible to filter off the product in the refluxing method in which water formed in the reaction was not removed.

#### EXAMPLE 11

50 To 100 g. of the same oil solution of an oil soluble calcium sulfonate as used in Example 1 were added 30 g. of calcium hydroxide, 5 g. of ethylene glycol and 50 g. of n-octyl alcohol, and gaseous carbon dioxide was blown thereinto at 140° C. with stirring under refluxing of n-octyl alcohol using a special refluxing tube for removing water, and water formed in the reaction was removed continuously therefrom, and the treatment was continued until the absorption of gaseous carbon dioxide ceased. After the completion of the reaction, the reaction mixture was maintained at 190° C. for an hour under a reduced pressure of 10 mm. Hg to remove the solvent and the reaction promoter therefrom. Thereafter, the unreacted inorganic material was removed by using a filter aid at a temperature in the vicinity of 150° C. to yield a product. The product was clear and dark brown in color and had the following properties:

65 Calcium content (wt. percent) ----- 12.2  
Basic value (mg. KOH/g.) ----- 308

In contrast, it was impossible to filter off the product in the refluxing method in which water formed in the reaction was not removed.

#### EXAMPLE 12

75 In 100 g. of the same oil solution of an oil soluble calcium sulfonate as used in Example 1 was suspended 30 g.

of calcium hydroxide, and to the resulting suspension were added 5 g. of ethylene glycol and 70 g. of isopropyl alcohol, and the resulting mixture was heated up to 87° C. with stirring and treated with gaseous carbon dioxide. Thereafter, the solvent, the reaction promoter and the unreacted inorganic material were removed according to the same procedures as in Example 1 to yield a product. The product was clear and had the following properties:

Calcium content (wt. percent)-----	11.7
Basic value (mg. KOH/g.)-----	294

In contrast, it was impossible to filter off the product in the refluxing method in which water formed in the reaction was not removed.

In order to investigate the performances of the lubricant additives having high ability of acid neutralization which are obtained in the process of this invention, these additives were incorporated to petroleum lubricant and the performances were evaluated by carrying out the bench tests described hereinafter.

As a result, it has been confirmed that the lubricant additives obtained in the process of this invention exhibit remarkable improvements in the ability of acid neutralization of lubricant for internal-combustion engines as well as in the engine cleaning performance as described in detail in the following examples.

#### EXAMPLE 13

An additive for lubricant obtained according to the process of this invention under the conditions described in Example 8 was incorporated to a petroleum lubricant having a viscosity of 199.7 cst. at 100° F. and 13.40 cst. at 210° F., and a viscosity index of 53.5 to evaluate the wear performance. As the testing engine, 2-cycle cross-head type Bolnes engine was used.

The test conditions, the compositions of the samples and the test results are as follows.

##### (1) Test conditions:

- Engine output power—80 BHP.
- Engine revolution—430 r.p.m.
- Temperature of water at the outlet of the cooling jacket—65° C.
- Temperature of lubricant at the outlet of the crankcase—61–62° C.
- Fuel oil—C-grade heavy oil.
- Temperature of fuel oil—80° C.
- Amount of cylinder oil supplied—1 g./hr./BHP. (per cylinder)

##### (2) Compositions of samples: <sup>1</sup>

- Sample A—Containing 10% by weight of an additive obtained according to the process of this invention.
- Comparative Sample B—Containing 15% by weight of commercially available calcium sulfonate scavenger.
- Comparative Sample C—Containing 20% by weight of commercially available calcium phenate scavenger.

##### (3) Test results:

The relative anti-wear values were evaluated by taking out the lubricant from the test engine in every 48 hours, measuring the iron content therein by fluorescence X-ray analysis and comparing the value with the average iron content in the standard oil.

Samples:

	Wear ratio <sup>2</sup>
A -----	0.8
B -----	1.2
C -----	1.3

<sup>1</sup> Based on the standard oil of which wear is 1. Thus, more wear than the standard oil gives the wear ratio of more than 1, and less wear than the standard oil gives the wear ratio of less than 1.

#### EXAMPLE 14

The detergent properties of the samples A, B and C specified in Example 13 were tested by using a Yammer

<sup>2</sup> All samples had basic values of 45 mg. KOH/g.

diesel engine (trade name). The test conditions and the results are as follows.

##### (1) Test conditions:

- Engine revolution—1500 r.p.m.
- Load—2.3 kg.
- Running time—120 hrs.
- Temperature of oil—52° C., min. 83° C., max. 65–75° C., ave.
- Temperature of water—70° C., min. 98° C., max. 90° C., ave.
- Temperature of exhaust—240° C., min. 470° C., max. 360° C., ave.
- Fuel used: Consisted of A-grade heavy oil (viscosity, 4.0 cst. at 50° C., residual carbon 0.2% by weight, sulfur content 1.17% by weight) and 5% by weight of di-tert-butyl disulfide.

#### TEST RESULTS

Samples	A	B	C
Piston ring sticking <sup>1</sup> -----	0	1.0	0
Detergency rating: <sup>2</sup>			
Crown land-----	0.1	0.8	0.4
Ring land (a)-----	0	0.1	0.6
Ring groove (b)-----	0	0	0.9
Piston skirt (c)-----	0	0.3	0.3
(a)+(b)+(c) <sup>1</sup> -----	0	0.4	1.8
Wearing amount of gearing (mg.)-----	9.1	30.7	41.6

<sup>1</sup> 0: best; 10: worst.

<sup>2</sup> Piston detergency rating is an evaluation on the basis of the amount and type of sludge and lacquer accumulated on the piston, giving zero point to the worst.

As can be clearly noted from the instant example, the lubricant additives obtained in the process of this invention show a remarkable improvement in performances of petroleum lubricant for the internal-combustion engines.

#### EXAMPLE 15

To a 500 cc. capacity four-necked flask charged with 300 g. of an oil solution of calcium petroleum sulfonate having a concentration of sulfonic acid of 0.060 mol percent, a molecular weight calculated as sodium sulfonate of 560, a calcium content of 2.3% by weight and a basic value of 16.4 mg. KOH/g. were added 90 g. of calcium hydroxide, 15 g. of ethylene glycol and 150 g. of a n-butanol, and into the resulting mixture was blown gaseous carbon dioxide at a rate of 300 ml./min. with stirring under reflux at 117° C. using a special refluxing tube provided for removing water, and water formed in the reaction was removed continuously therefrom. After the absorption of gaseous carbon dioxide ceased, n-butanol and ethylene glycol were removed and the remaining residue was filtered by using a filter aid to yield a product. The product was clear and dark brown in color and had the following properties:

Calcium content (wt. percent) -----	11.9
Basic value (mg. KOH/g.) -----	301
Viscosity (cst. at 98.9° C.) -----	150

To the product thus obtained was added 5% by weight of water, and the resulting mixture was heated up to 110–150° C. in the course of 40 minutes and then further heated up to 200° C. The resulting product was clear and had the following properties:

Calcium content (wt. percent) -----	11.9
Basic value (mg. KOH/g.) -----	300
Viscosity (cst. at 98.9° C.) -----	68

#### EXAMPLE 16

To a 300 cc. capacity four-necked flask charged with 100 g. of the same oil solution of calcium sulfonate as used in Example 15 were added 20 g. of calcium

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hydroxide, 5 g. of ethylene glycol and 70 g. of n-butanol, and into the resulting mixture was blown gaseous carbon dioxide at a rate of 160 ml./min. under reflux at 117° C. using a special refluxing tube provided for removing water, and the same procedures as in Example 15 were followed thereafter to yield a product.

To the product thus obtained were added freshly 20 g. of calcium hydroxide, 5 g. of ethylene glycol and 70 g. of n-butanol, and the same procedures as in Example 15 were followed thereafter to yield a product having the following properties:

Calcium content (wt. percent) -----	14.8
Basic value (mg. KOH/g.) -----	386
Viscosity (cst. at 98.9° C.) -----	250

To the product thus obtained was added 5% by weight of water, and the resulting mixture was heated up to 110–150° C. in the course of 30 minutes, and then further heated up to 200° C. The resulting product had the following properties:

Calcium content (wt. percent) -----	14.8
Basic value (mg. KOH/g.) -----	388
Viscosity (cst. at 98.9° C.) -----	103

## EXAMPLE 17

A 300 cc. capacity four-necked flask was initially charged with 100 g. of the product obtained in Example 15 which was not subjected to the water-heat treatment. There were added 15 g. of calcium hydroxide, 5 g. of ethylene glycol and 70 g. of n-butanol, and into the resulting mixture was blown gaseous carbon dioxide at a rate of 80 ml./min. with stirring under reflux at 117° C. using a special refluxing tube for removing water, and water formed in the reaction was removed continuously therefrom. After the absorption of gaseous carbon dioxide ceased, to the reaction mixture were freshly added 15 g. of calcium hydroxide and gaseous carbon dioxide was blown thereinto according to the same procedures as described above. After the absorption of gaseous carbon dioxide ceased, the unreacted inorganic material was filtered off and, subsequently, n-butanol and ethylene glycol were removed to yield a product. The product was clear and dark brown in color and had the following properties:

Calcium content (wt. percent) -----	18.8
Basic value (mg. KOH/g.) -----	505
Viscosity (cst. at 98.9° C.) -----	623

To the product thus obtained was added 5% by weight of water, and the resulting mixture was heated up to 110–150° C. in the course of 50 minutes and further heated up to 200° C. to yield a product having the following properties:

Calcium content (wt. percent) -----	18.8
Basic value (mg. KOH/g.) -----	507
Viscosity (cst. at 98.9° C.) -----	157

## EXAMPLE 18

Example 15 was repeated according to the same procedures as described therein except that monoethanolamine was substituted for ethylene glycol. As a result, a clear product having the following properties was obtained:

	Before water-heat treatment	After water-heat treatment
Calcium content (wt. percent)-----	12.1	121.
Basic value (mg. KOH/g.)-----	305	370
Viscosity (cst. at 98.9° C.)-----	161	71

## EXAMPLE 19

To a lubricant base having a specific gravity of 0.917 (15/4 C.), a viscosity of 13.4, a viscosity index of 53.5

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was incorporated each portion of 15% by weight of two types of the product obtained in Example 15, i.e. before and after the water-heat treatment, and the rust prevention test according to JIS K2510 and the anti-emulsification test were performed. The results are as follows:

Samples	Before treatment	After treatment
Rust prevention test.....	Unsatisfactory.....	Good.
Anti-emulsification test <sup>1</sup> (time required for emulsifying).	Emulsified in 3 minutes.	Not emulsified for 10 minutes.

<sup>1</sup> 100 cc. of sample and 100 cc. of distilled water were charged to a 250 cc. capacity sealed measuring cylinder and shaken with a shaking amplitude of 15 cm. and a shaking frequency of 140–150 times per minute and the time required for the emulsifying was measured.

What is claimed is:

1. A process for the production of a lubricant additive having a basic value higher than about 300, by one step which comprises reacting a mixture of an oil solution of oil soluble alkaline earth metal salt of sulfonic acid wherein the hydrocarbon portion has an average molecular weight of from 350 to 1,000 and at least one mol of an alkaline earth metal hydroxide per mol of said sulfonic acid with gaseous carbon dioxide in the presence of more than 25 percent by volume based on the volume of the starting oil solution of oil soluble alkaline earth metal salts of sulfonic acid of a member selected from the group consisting of a monohydric alcohol having not less than 3 carbon atoms, a petroleum solvent and a mixture thereof as a solvent, and further in the presence of a member selected from the group consisting of a dihydric alcohol, amino alcohol and alkylenediamine as a reaction promoter in the amount of less than 2 mols per mol of said sulfonic acid under refluxing conditions of said solvent while continuously removing water formed in the reaction from the reaction system, removing said solvent and said reaction promoter and unreacted inorganic material, and treating the remaining residue at a temperature 110° C. to 150° C. for 10 to 60 minutes in the presence of water, and thereafter heating to a temperature of 150° C. to 200° C. to distill off the water.

2. A process according to claim 1, wherein said oil soluble alkaline earth metal salt is Ca salt and said alkaline earth metal hydroxide is Ca hydroxide.

3. A process according to claim 1, wherein said remaining residue is treated at a temperature of 110° C. to 200° C. in the presence of from 3% to 15% by weight of said residue of water, and thereafter distilling off the water.

4. A process according to claim 1, wherein said promoter is a member selected from the group consisting of ethylene glycol, propylene glycol, butylene glycol, pentene glycol, hexene glycol and heptene glycol; aminoethanol, aminopropanol, aminobutanol and aminopentanol; and ethylene diamine, propylenediamine, butylenediamine, pentenediamine, hexenediamine and heptenediamine.

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U.S. Cl. X.R.

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