This invention relates to a method for preparing basic polyvalent metal salts of oil-soluble organic acids, particularly of oil-soluble petroleum sulfonic acids, naphthenic acids and alkyl-substituted salicylic acids. More specifically, this invention relates to the preparation of mineral oil solutions of highly basic alkaline earth metal petroleum sulfonates, naphthenates and alkyl-substituted salicylates.

It is well known that when a metal salt of an oil-soluble organic acid is prepared by the direct neutralization of the acid, the mere use of an excess of the neutralizing agent—generally the oxide, hydroxide or carbonate of the desired metal—may result in a product which contains an amount of metal in excess of that theoretically required to replace the acidic hydrogen atoms of the acid. These so-called "basic salts" have many uses, one of the most important being their use as components of compositions used as lubricants for internal combustion engines. These basic salts act as detergents, improving the lubricating properties of the compositions of which they are a part. Also, the excess metal appears to be present in the form of the original base used to neutralize the acid. This excess base imparts to the lubricating composition a characteristic commonly known as the "alkaline reserve." The alkaline reserve of a lubricating oil composition is an important factor in the effectiveness of the oil during operation, for apparently the excess base neutralizes sulfur and other acids formed during combustion of the fuel, reducing corrosion of the motor and decreasing wear of piston rings and cylinders.

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 \( \sigma \) percent by weight and if the content of metal in the mixture would have if it were present only as the normal salt is \( \beta \) percent by weight then the basicity of the mixture is

\[
\text{basicity} = \left( \frac{\sigma - \beta}{\beta} \right) \times 100\%
\]

With the demonstrated superiority of such basic salts over neutral or slightly acidic salts, many attempts have been made to increase the basicity of the salts. Generally, the proposed processes have involved the direct neutralization of the oil soluble organic acid with a large excess of the neutralizing agent. However, it has been found that there is a definite limit to the amount of basicity which may be imported into these salts by the proposed methods, and none of the proposals has been effective in producing salts having a basicity in excess of about 50-60%. Further, the basic salts prepared by these methods have often proven unstable, the basic material tending to separate from the salt—or from the lubricating composition—during storage.

It has now been discovered that salts of oil soluble acids having a basicity of 200% or more may be prepared by reacting an oil-soluble polyvalent metal salt of the organic acid, in the presence of a lower alkano, with a polyvalent metal carbonate formed in situ in the reaction mixture. The salts prepared by this method have proven to be highly stable, with substantially no separation of the basic material from the salt or lubricant composition during storage.

The process of the invention may be used to prepare highly basic polyvalent metal salts of such acids, as, for example, the cyclic sulfuric acids and carboxylic acids and the corresponding thio analogs. The process is particularly useful in the preparation of the highly basic salts of petroleum sulfonic acids, alkyl-substituted salicylic acids and naphthenic acids.

The sulfuric acids include the sulfonic acids, sulfuric acids, thiosulfonic acids, and the like. A particularly desirable group of these acids are the sulfonic acids, which term includes the aliphatic-substituted cyclic sulfonic acids in which the aliphatic substituent(s) contain a total of at least 12 carbon atoms, such as the allylarylsulfonic acids, allylalkylosulfonic acids, and alkyl-heterocyclic sulfonic acids, and aliphatic sulfonic acids in which the aliphatic radical contains at least 12 carbon atoms. Specific examples of oil-soluble sulfonic acids include: petroleum sulfonic acids; petroleum sulfonic acids; mono- and polywax substituted naphthalene sulfonic acids, substituted sulfonic acids such as cetyl-chlorobenzene sulfonic acids, cetylphenyl naphthalene sulfonic acids, substituted sulfonic acids such as petroleum naphthalene sulfonic acids, cetyl-cyclo-pentyl sulfonic acids, mono- and poly-wax substituted cyclo-hexyl sulfonic acids and the like.

The term, "petroleum sulfonic acids," is intended to cover all sulfonic acids which are derived directly from petroleum products.

The carboxylic acids include the cyclic types, such as those containing a benzenoid structure, and an oil-solubilizing radical or radicals, such as alkyl radicals containing a total of at least 12 carbon atoms. The cyclic type of carboxylic acids also includes cycloaliphatic carboxylic acids, such as the petroleum naphthenic acids, cetylcylohexane carboxylic acids, distearyl decanhydronaphthalene carboxylic acids, dioctylcylohexyl carboxylic acids, etc. The thio-carboxylic acids—i.e., such acids as mentioned above in which one or both of the oxygen atoms of the carboxylic acid group are replaced by sulfur—are also included.

A particularly desirable class of these carboxylic acids comprises the alkyl-substituted salicylic acids, especially those in which the alkyl groups are long-chain alkyl groups. The most desirable class of these acids comprises those which have been derived from benzene or phenol which has been alkylated with straight chain hydrocarbons with from about 8 to about 26, and preferably with from about 10 to about 22 carbon atoms. Alkyl-substituted salicylic acids of the kinds prepared by the processes disclosed in copending application Serial Number 444,394 (filed July 19, 1954, and now abandoned) are preferred members of this class of carboxylic acids.

The references herein to alkyl salicylic acids are intended to cover the individual acids and also mixtures of acids having different alkyl substituents, for example a mixture of alkyl salicylic acids having alkyl groups containing between 14 and 22 carbon atoms, for example...
a mixture of C_{11}-C_{18} mono- and di-alkyl salicylic acids. Mixtures of such acids, usually containing some alkyl phenol, will generally be used in practice and in many cases are to be preferred.

The polyvalent metal salt of the acid which is used as the starting material in the process of the invention may be prepared by directly neutralizing the acid with a polyvalent metal base. Alternatively, the polyvalent metal salt may be prepared by first neutralizing the acid with an alkali metal base, and then converting the alkali metal salt to the polyvalent metal salt by the metathetical reaction of the alkali metal salt with a polyvalent metal salt or base. The neutralization and/or metathesis reaction may be carried out using a solution of the oil soluble acid or alkali metal salt in a mineral oil. If desired, the polyvalent metal salt may be prepared in situ in the reaction mixture which is to be used in reacting the polyvalent metal salt with the polyvalent metal carbonate. In such case, the acid itself is used as the raw material, a polyvalent metal base being used to prepare the salt. This aspect of the process of the invention will be described in more detail hereinafter.

As the polyvalent metal base there may be used any basic compound of a polyvalent metal—by which is meant any compound of the polyvalent metal which is capable of neutralizing the oil-soluble organic acid. Most suitable are the polyvalent metal oxides, hydroxides and salts of the metal with a weak acid, such as the carbonate. As the polyvalent metal salt there may be used any water soluble salt of the polyvalent metal with a strong mineral acid. The salts of the polyvalent metal with the hydrohalic acids—the metal halides—are preferred. Of this group, the chlorides are preferred, since they are most widely available and least expensive.

The polyvalent metal may be any alkaline earth metal—i.e., strontium, calcium and barium.

The reaction of the polyvalent metal salt and the polyvalent metal carbonate formed in situ is carried out in the presence of any monohydric lower aliphatic alcohol. Preferably, the alcohol used boils below about 140° C. A preferred class of the monohydric lower aliphatic alcohols comprises the alkanols containing from 1 to about 6 carbon atoms. Examples of this class include methanol, ethanol and isopropanol, butanol and 2-propanol, n- and t-butyl alcohol, and the cyclic, cyclic C₆ and C₈ alcohols, both straight- and branched-chain in configuration. It is preferred that the alcohol be substantially water-miscible, and complete water-miscibility is desirable.

The polyvalent metal salt may be directly reacted with the polyvalent metal carbonate, or a solution of the salt may be used. Preferably, the salt is dissolved in a suitable solvent. Preferably, this solvent is hydrocarbon in character, and readily fluid at the reaction temperatures used. Such hydrocarbons as benzene, toluene or xylene are quite suitable, as are mixtures of one or more of these compounds. Gasoline fractions are also suitable, as are mineral oil fractions generally provided, their viscosity is not too high. Where the product of the reaction is to be a solution of the highly basic polyvalent metal salt to be used as an additive for lubricating oil compositions, the solvent should be compatible with the base fluid of the composition contemplated. Lubricating oil fractions having a viscosity of from about 100 to about 400 seconds Saybolt Universal at 50° C are suitable. Alternatively, where the solubilization, such as xylene or a gasoline fraction, is used, the solvent may be removed at the end of the reaction and replaced with the mineral oil, to provide a mineral oil concentrate of the highly basic polyvalent metal salt of the acid for use in lubricating oil compositions.

Where a solution of the polyvalent metal salt is used, care should be taken to use sufficient solvent to attain a readily fluid solution. In general, it is preferred that the salt be dissolved in at least an equal weight of solvent, and it is preferred that it be dissolved in from about one and one-half to about six times its weight of solvent.

The amount of the alcohol used should constitute at least five percent by weight of the organic acid, or alkali metal salt thereof, and it is preferred that several times this amount—from about 10% to about 75% by weight of the organic acid or alkali metal salt—be used. In some cases, a weight of alcohol equal to the weight of acid or alkali metal salt may be desirable. It will seldom be necessary to use more than about twice as much alcohol as acid or alkali metal salt (by weight).

The polyvalent metal carbonate is formed in situ by passing carbon dioxide into the reaction mixture containing free polyvalent metal base. Thus, where the polyvalent metal salt of the acid is used as the raw material, polyvalent metal base is added and carbon dioxide passed into the mixture; where the acid itself is the raw material, polyvalent metal base is added in an amount sufficient to provide an excess of base over the amount theoretically required to neutralize the acid. In any case, the amount of base added should be sufficient to provide at least two equivalents of free base in the reaction mixture per two equivalents of acid charged. It is desirable that the excess of base be so chosen with respect to the amount of carbon dioxide to be charged that an excess of base remains after carbonation is complete. In general, there should be a residual excess of base equal to at least about 5% by weight of the excess of base originally charged. For economic reasons, the residual excess of base should not exceed about 15% by weight of the excess of base originally charged.

The carbon dioxide may be added to the reaction mixture in any convenient manner. For example, the carbon dioxide may be bubbled through the mixture, or by injecting the reaction mixture into an atmosphere of carbon dioxide. It is preferred that the carbon dioxide be injected into the strongly agitated reaction mixture below the surface thereof, and that the reaction be conducted in a closed reactor, so that the reaction is also conducted in an atmosphere of carbon dioxide.

It has been found that, for a reaction mixture containing a certain excess of polyvalent metal base, as carbon dioxide is introduced into the reaction mixture the basicity of the product gradually increases; then, as the introduction of carbon dioxide continues, the basicity of the product suddenly begins to decrease. It has also been found that the stability of the product—the resistance of the product to precipitation of the excess base during storage—begins to rapidly decline at this same point. This phenomenon occurs while there is still free polyvalent metal base present in the mixture. This phenomenon, for which applicants at present have no sound explanation, is termed "overcarbonation."

Several methods have been devised for preventing this phenomenon:

(a) The amount of the alcohol affects it; the use of larger proportions of the alcohol to the polyvalent metal salt substantially reduces the danger of overcarbonation. Use of proportions of the alcohol within the preferred range heretofore stated virtually precludes overcarbonation.

(b) Control of the amount of polyvalent metal base used and the amount (fraction) of that base reacted with carbon dioxide, so that a residual excess of base exists, also reduces the hazard of overcarbonation. This factor has been discussed previously.

(c) The rate of carbon dioxide addition, and the speed with which the bulk of the reaction mixture is contacted with the carbon dioxide also affect the possibility of overcarbonation. It should be noted that overcarbonation may be a local as well as a general effect, so that the basicity of the product may be substantially reduced by allowing local overcarbonation to occur. Such may be prevented primarily by preventing the local amount of carbon dioxide from exceeding the local amount of base,
and by providing locally a sufficient amount of the alcohol. Effective dispersal of the gaseous and liquid components of the reaction mixture and correlation of the carbon dioxide addition rate with the degree of such dispersion is essential. Danger of local overcarbonation is also reduced by diluting the carbon dioxide with an inert gas, such as nitrogen, air, or water vapor.

(d) It has also been found that the presence of substantially amounts of water in the reaction zone increases the danger of overcarbonation. Therefore, it is desirable that the reaction mixture be substantially anhydrous. The effect of the water on overcarbonation, has, however, been found to be much less where a large proportion of the alcohol is used. In the case where the weight ratio of the alcohol to the polyvalent metal salt lies at about 50%—from 5% to about 65%—by weight of the organic acid or salt charged an amount of water amounting to as much as 15% by weight of the reaction mixture may be present without danger of overcarbonation. The proportion of water in the reaction mixture should, therefore, be maintained below this limit; where high alcohol/polyvalent metal salt weight ratios exist. Where the weight ratio is substantially below about 50%—i.e., below about 25% the amount of water permissible is correspondingly lower, preferably not more than about 2 to about 5 percent by weight of the reaction mixture.

The reaction temperature should not exceed about 70°C., and the attainment of reasonable reaction rates requires that temperatures of at least 20°C. be used. It is preferred that the reaction temperature lie between about 30°C. and about 70°C. If the temperature exceeds this limiting value, the rate of carbon dioxide absorption becomes so low that feasibly low reaction rates result. Although the reaction may be carried out at any pressure above atmospheric pressure, it has been found unnecessary to employ pressures above about five pounds per square inch, gauge. In most cases, operation at substantially atmospheric pressure is satisfactory. The reaction time is not a critical factor in the process of the invention. In general, a reaction of at least ½ hour is required but it seldom exceeds about 4–5 hours. In most cases a reaction time of from about ½ hour to about 2 hours will be required.

The reaction mixture at the end of the reaction contains the highly basic polyvalent metal salt, some free polyvalent metal carbonate, some unreacted polyvalent metal base, the alcohol, possibly some water, hydrocarbon diluent (if such were used), and possibly other inorganic salts. The metal carbonate, metal base, and other inorganic salts are present in the solid form, and may be removed by centrifuging or filtering the reaction mixture. The alcohol and the water can be removed by distillation. A final filtration may be used to remove any traces of solid matter. Where a volatile hydrocarbon diluent was used, this, too, may be removed by distillation.

The process of the invention may be operated in a batch manner, or it may be operated in a cyclic, including continuous, manner. When the process is operated in a cyclic manner, the sludge obtained by filtration of the reaction mixture, which sludge comprises primarily polyvalent metal carbonate and polyvalent metal base, may be used to neutralize the organic acid, or to metabolically replace the alkali metal from the salt thereof.

The following examples are offered as illustrations of some specific applications of the process of the invention:

Example I

A mixture of highly basic calcium alkyl salicylates (C15-C18 mono- and di-alkyl salicylates) was prepared using a reaction vessel fitted with a stirrer, a reflux condenser and means for bubbling carbon dioxide through the reaction mixture.

At the commencement of the process 1500 parts by weight of a 70% solution of alkyl salicylic acids in xylene (C14-C18 mono- and di-alkyl salicylic acids containing 75% some unreacted alkyl phenol and having an acid value about 50 mg. KOH/g.) were placed in the reaction vessel, together with 5%, by weight of the acid solution of methanol and 200 parts, by weight (i.e., four equivalents) of calcium hydroxide. The resulting mixture was then heated to 60°C. with vigorous stirring (1500–2000 rpm) and maintained at that temperature for ½ hour, whereupon carbon dioxide was bubbled through the reaction mixture, which was maintained at 60°C. and stirred vigorously throughout.

The reaction mixture was then centrifuged to remove any unreacted calcium hydroxide and any calcium carbonate produced during the course of the reaction and not utilized in producing the highly basic product, and the resulting liquid was distilled to remove the xylene, the water produced in the course of the reaction and some of the xylene. The remaining xylene solution was clarified by filtration and a quantity of spindle oil was then added to the clarified solution and the xylene removed therefrom by distillation leaving a concentrated spindle oil solution of the highly basic calcium alkyl salicylates.

The resulting mineral oil concentrate was used as additive for lubricating oils with which it was found to have excellent blend stability. Blend stability may also be determined by diluting a sample of the xylene solution with about 25 parts by volume of pentane. Stable material gives a completely clear and bright solution in this test. The highly basic calcium alkyl salicylates produced in the foregoing process yielded a pentane-diluted solution which was clear and bright when observations were made at the end of nine weeks.

The highly basic product was found to have a basicity of about 226%; its total base and acid contents being 3.87 and 1.19 mili-equivalents per gram respectively.

Example II

The process of Example I was repeated using 10%, by weight of the acid solution, of methanol and a reaction temperature of 60°C.; other conditions remaining substantially the same.

A highly basic product having a basicity of about 266% and a total base and acids content of 3.85 and 1.05 mili-equivalents per gram respectively was obtained. The resulting mineral oil concentrate had excellent blend stability with lubricating oils, the pentane-diluted solution being clear and bright when observations were made at the end of nine weeks.

Example III

A mixture of highly basic calcium alkyl salicylates (C15-C18 mono- and di-alkyl salicylates) was prepared by a continuous process using two reaction vessels each fitted with a stirrer and a reflux condenser and connected in series with an intermediate surge vessel. The second reaction vessel was also provided with means for bubbling carbon dioxide through the reaction mixture therein.

A slurry comprising a 70% solution in xylene of C14-C18 mono- and di-alkyl salicylic acids containing some unreacted alkyl phenol (by weight of the acid solution) of methanol and four equivalents of calcium hydroxide was charged into the first reaction vessel in which the temperature of the slurred reaction mixture was raised to 60°C. and maintained at that temperature for ½ hour, with constant vigorous stirring. The resulting mixture, which contained basic calcium alkyl salicylates of about 50% basicity, was then passed to the surge vessel from which it was fed continuously into the second reaction vessel in which the highly basic product was produced, in accordance with the invention, by forming calcium carbonate in situ in the reaction mixture by bubbling in carbon dioxide with constant vigorous stirring. The feed rate of the reaction mixture from the surge vessel to the second reaction vessel was 0.35 volume per second and carbon dioxide was bubbled through at the rate of 6.9 volumes per second, the reaction mixture being main-
tained at 60° C. Reaction mixture was withdrawn con-
tinuously from the second reaction vessel at a rate such
that the average residence time therein was 1/2 hour.
A highly basic product having a basicity of about
208% was obtained. The reaction mixture was worked
up in the manner described in Example I to give a mineral
oil concentrate having excellent blend stability with lubri-
cating oils.

Example IV
The continuous process of Example III was repeated
using 10% by weight of the acid solution, of methanol
and a reaction temperature of 60-65° C. in both reaction
vessels. The reaction mixture was fed from the surge
vessel to the second reaction vessel at the rate of 0.5 l
volumes per second and carbon dioxide was fed thereto at
the rate of 8.3 volumes per second.
A highly basic product having a basicity of about
202% was obtained. The reaction mixture was worked up
in the manner described in Example I to give a mineral
oil concentrate having excellent blend stability with lubri-
cating oils.

The various highly basic calcium alkyl salicylates pro-
duced in accordance with the foregoing Examples I to IV
were subjected to engine performance tests as additives
for Carboron HVI 170 base lubricating oil. (Carboron HVI 170 oil is a Duosol extracted lubricating fraction of about
100 viscosity index and having a viscosity of 170 second
Redwood No. 1 at 140° F.) Good results were obtained
in the Gardner engine piston-cleanness test (comparable
to CRC Designation L-1-545), the Fowler ring sticking
test the Chevrolet L-4 test (CRC Designation L-4-545)
and the Peter engine LA3A test (CRC L-3-545). In
addition, these highly basic calcium alkyl salicylates were
found to have excellent compatibilty and blend stability
at 100° C. with a number of different lubricating oils,
both in the absence and in the presence of other addi-
tives, such as octyl formol and Anglimol 304, a crank-
case oil corrosion and oxidation inhibitor manufactured
by The Lubrizol Corporation.

Example V
A mixture of highly basic calcium alkyl salicylates
(C12-C18 mono- and di-alkyl salicylates) was prepared
using a reaction vessel fitted with a stirrer, a reflux con-
denser and a means of circulating a mixture of carbon
dioxide and air through the reaction mixture.
At the commencement of the process, 1,000 parts by
weight of a 70% solution of alkysalicylic acids (C16-C18
mono- and di-alkyl salicylic acids containing some unreac-
ted alkyl phenol and having an acid value of 57 mg.
KOH/g.) in xylene were placed in the reaction vessel
with 10%, by weight of the acid solution, of
methanol (i.e., 100 parts by weight) and 532 parts by
weight of calcium hydroxide (i.e., 14 equivalents per
equivalent of alkyl salicylic acids). The resulting mix-
ture was stirred for 30 minutes during which the tempera-
ture rose to 30° C. A mixture of air and carbon di-
oxide containing 40% (by volume) of carbon dioxide
was then circulated through the reaction mixture, at the
rate of about 300 liters/hour, the reaction mixture being
vigorously stirred (1800 R. P. M.) and carbon dioxide
being added to the cycling gas at the same rate as carbon
dioxide was absorbed by the reaction mixture. The ab-
sorption was continued for 34 minutes during which time
the reaction mixture absorbed 67 liters of carbon dioxide
and its temperature rose from 30° C. to 60° C. The
mixture was then stirred for 24 hours before diluting
with xylene and centrifuging to remove the unreacted
solids. The resulting liquid was distilled to remove the
methanol, the water produced in the reaction and some
of the xylene. The remaining xylene solution was filtered
and the xylene removed by distillation leaving the highly
basic calcium alkylsalicylates.

The highly basic product was found to have a basicity
of about 512%; its total base and acid contents being
5.12 and 0.836 milliequivalent per gram respectively.

Example VI
The process of Example V was repeated using 575
parts by weight of the acid solution, 517 parts by weight
of methanol, 55 parts of water and 89 parts of calcium
hydroxide (4 equivalents per equivalent of alkyl salicylic
acids). The reaction mixture was first stirred for 30
minutes during which time the temperature rose to 25°
C., whereupon a 20% carbon dioxide/air mixture was
circulated through the reaction mixture at the rate of
600 liters/hour for 16 minutes. During this period 12
litres of carbon dioxide were absorbed and the tempera-
ture of the reaction mixture rose to 32° C. The reaction
mixture was stirred for a further 24 hours and the unreac-
ted solids removed by centrifuging. The remaining
liquid separated into two phases and the lower xylene
phase containing the highly basic calcium alkylsalicylates
was distilled to remove methanol, water and some xylene.
The remaining xylene solution was filtered, a quantity of
spindle oil was added and the remaining xylene was then
removed leaving a concentrated spindle oil solution of
highly basic calcium alkyl salicylates having a basicity
of 226%.

Example VII
The process of Example V was repeated using 971 parts
by weight of the acid solution, 97 parts by weight of
methanol and 151 parts by weight of calcium hydroxide
(4 equivalents per equivalent of alkyl salicylic acids).
The reaction mixture was heated to 50° C. and stirred at
this temperature for 5 minutes. A 20% by volume car-
don dioxide/air mixture was circulated through the re-
action mixture at the rate of 600 liters/hour for 43
minutes during which period the mixture absorbed 20
litres of carbon dioxide. The reaction mixture was stirred
for 24 hours and the resulting highly basic calcium alkyl-
salicylates were obtained in the manner described in Ex-
ample V. The product had a basicity of 222%.

Example VIII
The process of Example V was repeated using a 35%
solution in xylene of C16-C18 mono-di-alkyl salicylic
acids having an acid value of about 30 mg. KOH/g.
1105 parts by weight of acid solution, 57.5 parts by
weight of methanol and 87.5 parts by weight of calcium
hydroxide (4 equivalents per equivalent of alkyl salicylic
acids) were mixed together for 30 minutes. A 20% by
volume carbon dioxide/air mixture was then circulated
through the reaction mixture for 20 minutes during which
time 12.2 litres of carbon dioxide were absorbed. The
reaction mixture was then stirred for 24 hours and the
highly basic calcium alkylsalicylates, which were ob-
tained in the manner described in Example V, had a
basicity of 185%.

The process of the present invention is also equally
applicable to the preparation of other oil-soluble highly
basic polyvalent metal salts of for example naphthenic
acids and petroleum sulfonic acids, i.e., sulfonic acids
or mixtures thereof which are derived directly from petro-
leum products, as is illustrated by the following examples:

Example IX
3.3 kilograms of naphthenic acids (acid value 170
mg./KOH per gram) dissolved in 7.6 gallons of xylene
were mixed with a slurry containing 50% w/w of calcium
dioxide and 7 kilograms of methanol in the
reaction vessel used in Example I. After mixing with
continuous high speed stirring for 1 hour at 60°
C., the system was flushed free from air and about 40
cubic feet of carbon dioxide was bubbled through the
reaction mixture over a period of 4 hours. The tem-
perature during the carbon dioxide treatment was 35-
40° C.

The resulting reaction product was then filtered at
room temperature through a filter pre-coated with Clarcel filter aid to remove suspended solids and the clear filtrate was then added to a light hydrocarbon oil base and the methanol and xylene were removed by distillation, together with the water formed during the reaction, to give a solution of highly basic calcium naphthenates in oil. The basicity of the product was about 100%.

### Example X

66 parts by weight of naphthenic acids (acid value 170 mg. KOH/g.) dissolved in 600 parts by weight of xylene were mixed with a slurry comprising 72.7 parts of barium oxide and 4 parts of methanol in a reaction vessel as described in Example I. After mixing with continuous high speed stirring for 2 hours the system was flushed free from air and 0.323 cubic foot of carbon dioxide at 100 cm. Hg pressure and 20°C. was bubbled through the reaction mixture during a period of 12 minutes. The temperature during the carbon dioxide treatment was about 30°C.

The resulting reaction product was then filtered at room temperature through a filter precoated with Clarcel filter aid to remove suspended solids and the resulting xylene solution of highly basic barium naphthenates was found to have a basicity of 252%.

### Example XI

A mineral oil solution of highly basic calcium petroleum sulfonates was prepared from the acid oil obtained by saponifying "Cardon 65" (a solvent refined lubricating oil having a viscosity of about 65 seconds Redwood 1 at 140°F. and a viscosity index of about 95), the acid oil having an acid value of 21.5 mg. KOH per gram and a sulfonic acid content of 12.5% by weight.

The acid oil was neutralized with excess calcium hydroxide at 40°C. The calcium hydroxide was added in the form of a slurry with 99% methanol so as to yield a mixture containing 5 equivalents (based on the sulfonic acids content of the acid oil) of free calcium hydroxide and 10%, by weight of the acid oil of methanol. Altogether 3.5% of calcium hydroxide by weight of the acid oil was added.

The resulting mixture was then stirred vigorously (3000 R. P. M.) at 40-42°C. for 1 hour during which time carbon dioxide was bubbled through the mixture, about 1.8% of carbon dioxide, by weight of the acid oil (75% equivalent based on the free calcium hydroxide) being absorbed. The reaction product yielded on filtration a 12.5% mineral oil solution of basic calcium petroleum sulfonates which was of good color and had a viscosity of 94 centistokes at 100°F. It had an alkalinity of 34 mg. KOH per gram, a sulfated ash content of 6.2% and a control ratio of 5.5.

The term, "control ratio" is defined as follows:

\[
\text{Alkalinity (mg. KOH/g of concentrate)} = \text{Percent sulfated ash} - h
\]

In the above expression, and as used throughout the present specification, the terms "alkalinity" and "basicity" mean "total base number," determined by electrometric titration according to American Society for Testing Materials, Designation D664-49. By this test, metal hydroxides, such as calcium hydroxide, and salts of metals with weak acids, such as calcium carbonate, have equal alkalinity on a mole-for-mole basis. Sulfate ash is determined by first igniting the sample until only ash and carbon remain, then heating with sulfuric acid at 260°C. until all of the carbon is oxidized, cooling, and reheating with sulfuric acid, and then igniting to 415°C.

This test, the official name of which is "Sulfated Residue," is detailed in American Society for Testing Materials, Designation D874-47T.

In this specification, the terms "neutral salt," "basic salt," and "highly basic salt" have been used. These terms are intended to have the meaning set out for these terms in United States Patent No. 2,585,520, issued February 12, 1952, to Paul Van Es and Hubert Sipple. Briefly, the "neutral salt," is the salt represented by the formula M(R)₂, wherein M represents the metal, R represents the acid residue and x represents the valence of the metal. Thus, the neutral salts are those wherein all of the valences of the metal are satisfied by acid residues. The "basic salts" are those represented by the formula: M(OH)₄(R)₉, wherein M, and R have the meaning above and a+b=x the valence of the metal. In those salts, one or more but less than all of valences of the metal are satisfied by hydroxyl radicals, the remaining valence(s) by acid residues. The "highly basic salts" are those in which the basicity is greater than the basicity of the basic salts, the excess basicity being present in the form of the free base, or as a complex of the base with the sulfonate.

It will be noted that in the highly basic salts prepared according to this invention, the excess base is present primarily in the form of the metal carbonate, and not in the form of the metal hydroxide. These salts thus are essentially neutral in solution—i.e., they have a pH substantially above 7.0—but are capable of neutralizing substantially larger amounts of acids than are the basic salts available heretofore. Highly basic salts of this kind are highly desirable for many applications where the pH of the salt must not vary substantially from 7.0, as where the salt is added to lubricant compositions containing other additives which may not tolerate a pH above about 7.0.

We claim as our invention:

1. A process for preparing an oil soluble highly basic metal salt of an organic acid, said process comprising reacting, as the only chemically reactive organic material, an oil soluble organic acid compound selected from the class consisting of (1) cyclic sulfur acids containing at least 18 carbon atoms per molecule, (2) cyclic carboxylic acids containing at least 17 carbon atoms per molecule, and (3) salts of those acids with alkali metals and with alkaline earth metals, in the presence of at least 5% of the weight of said organic acid compound of a lower alkali, with an alkaline earth metal carbonate formed in situ, by the reaction of carbon dioxide and an alkaline earth metal base, at least a part of said base being in the free state, thereafter removing said alkali and any water present in the resulting mixture.

2. A process for preparing an oil soluble highly basic metal salt of an organic acid, said process comprising reacting, as the only chemically reactive organic material, an oil soluble organic acid compound selected from the class consisting of (1) cyclic sulfuric acids containing at least 18 carbon atoms per molecule, (2) cyclic carboxylic acids containing at least 17 carbon atoms per molecule, and (3) salts of those acids with alkali metals and with alkaline earth metals, said oil soluble organic acid compound being in solution in a hydrocarbon oil, in the presence of at least 5% by weight of said organic acid compound of a lower alkali, with an alkaline earth metal carbonate formed in situ by the reaction of carbon dioxide and an alkaline earth metal base, at least a portion of said metal base being in the free state, and thereafter removing said alkali and any water present in the resulting mixture.

3. A process according to claim 2 wherein the amount of carbon dioxide reacted is less than the amount theoretically required to convert the free alkaline earth metal base to the corresponding alkaline earth metal carbonate.

4. A process for preparing an oil soluble highly basic metal salt of an alkyl-substituted salicylic acid, said process comprising mixing a hydrocarbon oil solution containing as the only chemically reactive material an oil soluble alkaline earth metal salt of an alkyl-substituted salicylic acid in which each alkyl group contains at least eight carbon atoms, with at least 5% of the weight of the said salt of a lower alkali, and with an alkaline earth metal base,
at least a part of said base being in the free state, adding carbon dioxide to the resulting mixture and thereafter removing said alkanol and any water present in the resulting mixture.

5. A process according to claim 4 wherein the alkaline earth metal salt of the alkyl-substituted salicylic acid is formed in situ by reaction of the alkyl-substituted salicylic acid and an alkaline earth metal base.

6. A process for preparing an oil soluble highly basic metal salt of petroleum sulfonic acid, said process comprising mixing a hydrocarbon oil solution consisting as the only chemically reactive material an oil soluble alkaline earth metal salt of a petroleum sulfonic acid with at least 5% of the weight of the said salt of a lower alkanol, and with an alkaline earth metal base, at least a part of said base being in the free state, adding carbon dioxide to the resulting mixture and thereafter removing said alkanol and any water present in the resulting mixture.

7. A process according to claim 6 wherein the alkaline earth metal salt of the petroleum sulfonic acid is formed in situ by reaction of the petroleum sulfonic acid and an alkaline earth metal base.

8. A process according to claim 6 wherein the amount of carbon dioxide reacted is less than the amount theoretically required to convert the free alkaline earth metal base to the corresponding alkaline earth metal carbonate.

9. A process according to claim 6 wherein the alkaline earth metal salt of the petroleum sulfonic acid is formed in situ by reaction of an alkali metal salt of the petroleum sulfonic acid and an alkaline earth metal base.

10. A process for preparing an oil soluble highly basic metal salt of a napthenic acid, said process comprising mixing a hydrocarbon oil solution containing as the only chemically reactive material an oil soluble alkaline earth metal salt of a napthenic acid with at least 5% of the weight of the said salt of a lower alkanol, and with an alkaline earth metal base, at least a part of said base being in the free state, adding carbon dioxide to the resulting mixture and thereafter removing said alkanol and any water present in the resulting mixture.

11. A process according to claim 6 wherein the alkaline earth metal salt of the napthenic acid is formed in situ by reaction of the napthenic acid and an alkaline earth metal base.

References Cited in the file of this patent

UNITED STATES PATENTS

2,304,230 Archibald et al. .......... Dec. 8, 1942
2,617,049 Asseff et al. .......... Nov. 4, 1952
UNITED STATES PATENT OFFICE
CERTIFICATION OF CORRECTION

Patent No. 2,865,956

Glyn Ellis et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 2, line 34, for "sulwonic" read -- sulfonic --;
line 36, strike out "naphthalene sulfonic acids, substituted sulfonic acids" and insert instead -- sulfonic acids, and the like; cycloaliphatic sulfonic acids, --; line 37, for "such at" read -- such as --.

Signed and sealed this 6th day of June 1961.

(Seal)
Attest:

ERNEST W. SWIDER
Attesting Officer

DAVID L. LADD
Commissioner of Patents
Notice of Adverse Decision in Interference

In Interference No. 91,510 involving Patent No. 2,865,956, G. Ellis, J. Hartley and J. C. Moseley, Preparation of basic polyvalent metal salts of organic acids, final judgment adverse to the patentees was rendered Feb. 20, 1963, as to claims 1, 2, 3, 4, 5, 6, 7, 8, 9 and 10.

[Official Gazette April 30, 1963.]