United States Patent Office 3,014,866 Patented Dec. 26, 1961

3,014,866

LUBRICATING OIL COMPOSITIONS

Richard L. Ferm, El Cerrito, Calif., assignor to California Research Corporation, San Francisco, Calif., a corporation of Delaware

No Drawing. Filed Dec. 29, 1958, Ser. No. 783,084
5 Claims. (Cl. 252—33)

This invention pertains to lubricating oil compositions having improved viscosity index characteristics; in particular, this invention is directed to certain particular metal sulfonates which are effective in improving the viscosity temperature characteristics of lubricating oil compositions. The particular metal sulfonates described herein are effective to improve the viscosity-temperature characteristics, that is, the viscosity index (V.I.) of lubricating oil compositions.

The greater proportion of oils obtainable by refining processes and useful as base oils for lubricating oil compositions have wide variations in viscosity characteristics with changes in temperature. They do not have agents naturally embodied therein for the purpose of imparting reduced changes in viscosity with changes in temperature. That is, at a particular temperature, a lubricating oil may be quite viscous, while at higher temperatures the lubricating oil may have a viscosity of a fluid, such as a distillate. In order that the viscosity of a lubricating oil composition will not change rapidly with changes in the temperature of an internal combustion engine, for example, numerous additives have been designed to modify the viscosity-temperature characteristics of lubricating oils. The changes in the viscosity occurring with variations in temperatures are kept at a minimum.

Polymeric additives in general are used to improve the viscosity index characteristics of lubricating oil compositions. Such polymeric additives include, for example, alkyl methacrylate polymers (e.g., polybutyl methacrylate), and polyolefins (e.g., polybutene). Although these additives improve the viscosity-temperature relationships of lubricating oils, there is a lack of compatibility between such V.I. improving agents with other lubricating oil additives. In some instances, the polymeric V.I. improving agents form complexes with other additives.

Although the art is replete with V.I. improving agents for lubricating oil compositions, for the most part, such improving agents are relatively costly, as compared to the base oil itself.

It is a primary object of this invention to set forth lubricating oil compositions having incorporated therein new viscosity index improving agents which have greater thickening properties than the viscosity index improving agents of the prior art.

It is a further object of this invention to set forth new lubricating oil viscosity index improving agents which are less costly than those heretofore available, and which are more compatible with available lubricating oil additives useful as oxidation inhibitors, corrosion inhibitors, etc., than the V.I. improving agents of the prior art.

In accordance with this invention, it has been discovered that double carbonated, double basic barium sulfonates are effective for improving the viscosity-temperature characteristics (i.e., the V.I.) of lubricating oil compositions. Thus, the compositions of this invention comprise oils of lubricating viscosity and double carbonated, double basic barium sulfonates.

The particular carbonated basic barium sulfonates of this invention are not only more compatible with other lubricating oil additives, than presently used V.I. improving agents, for example, detergents, oxidation inhibitors, etc., the new V.I. improving agents described herein also reduce the pour point of lubricating oils.

It is well known that basic metal sulfonates are useful

as detergents in lubricating oil compositions. For example, McNab Patent No. 2,418,894 and Mertes Patent No. 2,501,731 therefore teach the use of basic metal sulfonates as detergents in lubricating oil compositions. Furthermore, in numerous patents (e.g., in Patent No. 2,616,904) Asseff teaches that carbonated basic metal sulfonates are detergents for lubricating oil compositions. However, the particular barium sulfonates of this invention affect lubricating oil compositions in a manner just contrary to that of the prior art metal sulfonates. Whereas, the known metal sulfonates are detergents, that is, serve as dispersing agents in lubricating oil compositions, eliminating the formation of heavy deposits, the particular metal sulfonates described herein actually thicken lubricating oils.

As used herein, the term "double carbonated sulfonate" will be used to mean "double carbonated-double basic barium sulfonate."

Double carbonated, double basic barium sulfonates are obtained by the formation of neutral barium sulfonates, from which basic barium sulfonates are obtained. These basic barium sulfonates are carbonated, and the resulting carbonated basic barium sulfonates are reacted further with barium oxide (or hydroxide), followed by further carbonation.

The carbonation may be accomplished by the use of carbon dioxide gas or by the use of urea, which when reacted with barium oxide (or hydroxide) results in the formation of carbon dioxide.

The double carbonated sulfonates can be prepared from neutral metal sulfonates represented by the formulas

$$(RSO_3)_2Ba$$

and

$$[(R)_aASO_3]_2Ba$$

wherein R is a high molecular weight cyclic, straight-chained or branch-chained saturated or unsaturated essentially hydrocarbon radical having a molecular weight ranging from about 150 to about 800; A is an aromatic radical, such as benzene, naphthylene, anthracene, biphenyl, etc.; and *a* is a number having a value of 1 to 4.

Examples of suitable hydrocarbon radicals are the following: dodecane, hexadecane, eicosane, triacontane radicals; radicals derived from petroleum hydrocarbons, such as white oil, wax, olefin polymers (e.g., polypropylene and polybutylene, etc.). The sulfonic acids used in preparing the oil soluble metal sulfonates of this invention also include the oil soluble sulfonic acids derived from petroleum, such as the "mahogany" acids, and the synthetic sulfonic acids prepared by various methods of synthesis (e.g., sulfonic acids prepared by reacting a chlorinated white oil with benzene, using hydrofluoric acid as a catalyst, then treating the resulting white oil alkylated benzene with chlorosulfonic acid or fuming sulfuric acid to form a white oil benzene sulfonic acid).

The barium sulfonates which are used in the formation of the carbonated basic sulfonates herein are exemplified as follows: barium white oil benzene sulfonate, barium dipolypropene benzene sulfonate, barium mahogany petroleum sulfonate, barium triacontyl sulfonate, etc.

In the preparation of the double carbonated double basic barium sulfonates of this invention, it is desirable that the reactants are preesnt in certain particular mol ratios to obtain the desired lubricating oil thickening action. The specific mol ratios of the various reactants used in the formation of the double carbonated barium sulfonates of this invention are set forth hereinbelow as follows:

In the preparation of the basic sulfonates, the amount of barium hydroxide (or oxide) is at least 0.5 mol in excess of that necessary for the formation of a neutral

metal salt of a sulfonic acid. It is preferred that the basic sulfonate contains from 1 to 1.5 mols of barium in excess of that necessary for the formation of a neutral barium sulfonate. The resulting basic barium sulfonate is then reacted with CO_2 in an amount of 0.5 to 1.0 mol of CO_2 per mol of basic barium content of the sulfonate. This carbonated basic sulfonate is then further reacted with 1 mol to 1.5 mols of barium hydroxide (or oxide), followed by further reaction with CO_2. With regard to the initial carbonation, for each mol of basic barium content in the sulfonate, it is critical to use from 0.5 to 1.0 mol of carbon dioxide, followed by reaction with from 1 to 1.5 mols of barium hydroxide (or oxide), then finally with from 0.5 mol to 1 mol of CO_2 per mol of additional barium incorporated being preferred.

In the carbonation step, it is preferred that the temperatures be at least 250° F., that is, from 250° F. to 400° F. and higher, at atmospheric pressures.

In the formation of lubricating oil compositions containing the carbonated barium sulfonates of this invention, the lubricating oil composition contains an amount thereof sufficient to improve the viscosity index of the base oil, which amount may be from 0.5%, by weight, to 25%, by weight; with 3%, by weight, to 8%, by weight being preferred.

Lubricating oils which are suitable herein as base oils for the compositions of this invention, the viscosity-temperature characteristics of which oils are improved by the double carbonated, double basic metal sulfonates described herein, include a wide variety of lubricating oils, such as naphthenic base, paraffin base, and mixed base lubricating oils, other hydrocarbon lubricants, e.g., lubricating oils derived from coal products, and synthetic oils, e.g., alkylene polymers (such as polymers of propylene, butylene, etc., and the mixtures thereof), alkylene oxide-type polymers, dicarboxylic acid esters, liquid esters of acids of phosphorus, alkyl benzenes, polyphenyls (e.g., biphenyls and terphenyls), alkyl biphenyl ethers, etc. Synthetic oils of the alkylene oxide-type polymers which may be used include those exemplified by the alkylene oxide polymers (e.g., propylene oxide polymers) and derivatives, including alkylene oxide polymers prepared by polymerizing the alkylene oxide, e.g., propylene oxide, etc., in the presence of water or alcohols, e.g., ethylene alcohol, esters of ethylene oxide-type polymers, e.g., acetylated ethylene oxide polymers prepared by acetylating ethylene oxide polymers containing hydroxyl groups; polyethers prepared from ethylene glycols, e.g., ethylene glycol, etc.

Synthetic oils of the dicarboxylic acid ester type include those which are prepared by esterifying such dicarboxylic acids as adipic acid, azelaic acid, suberic acid, sebacic acid, alkanol succinic acid, fumaric acid, maleic acid, etc., with alcohols such as butyl alcohol, hexyl alcohol, 2-ethyl hexyl alcohol, dodecyl alcohol, etc.

Synthetic oils of the aromatic type include those which are prepared by alkylating benzene (e.g., monoalkyl benzene such as dodecyl benzene, tetradecyl benzene, etc., and dialkyl benzenes (e.g., n-nonyl 2-ethyl-hexyl benzene); aryl esters (e.g., bis(carbethoxydecyl) benzene, 2-ethylhexyl phenyl decanoate, bis(carbethylhexoxydecyl) benzene, etc.). Other aryl type synthetic oils include indane and derivatives thereof (e.g., 1,1,3-trimethyl-3-phenyl indane; 1,1,3-trimethyl-3-n-nonyl phenyl indane, etc.); bis(phenoxyphenyl) alkanes (e.g., bis(phenoxyphenyl) nonane, etc.); polyaryl alkanes (e.g., bis(diphenylyl) nonane, phenyl (n-nonylphenyl) isodecane, diphenyl decane, etc.); polyalkyl terephenyls; alkyl dipenyl ethers, etc.

Synthetic oils of the type of polymers of silicon include the esters of silicon and the disiloxanes which include those exemplified by tetraethyl silicate, tetraisopropyl silicates, tetra (4-methyl-2-tetra ethyl) silicate, hexyl (4-methyl-2-pentoxy) disiloxane, poly(methyl) siloxane, poly (methyl phenyl) siloxane, etc.

The above base oils may be used individually or in combination thereof, whenever miscible or wherever made so by the use of mutual solvents.

The following examples illustrate the formation of carbonated basic barium sulfonates in accordance with this invention.

EXAMPLE I

Preparation of a neutral barium sulfonate from a neutral calcium sulfonate

A mixture of 3,234 grams of a lubricating oil concentrate of a calcium petroleum sulfonate (which concentrate contains a total of 1.66%, by weight, of calcium) (wherein the petroleum radical of the sulfonate was derived from a California solvent refined paraffinic base oil having a viscosity of 480 SSU at 100° F.) and 3,200 ml. of Standard, 350 petroleum thinner was heated to 170° F., to which mixture was further added an aqueous solution of 453 grams of barium chloride dihydrate in 1200 ml. of water. This two-phase mixture was agitated violently for a period of two hours at 170° F.–180° F. The solvent solution of the sulfonate was separated, and subsequently treated with an aqueous solution of 453 grams of barium chloride dihydrate in 1200 ml. of water as described hereinabove. Again, the solvent solution of the sulfonate was recovered and further treated similarly with an aqueous phase of 453 grams of barium chloride dihydrate in 1200 ml. of water. After the third treatment with barium chloride dihydrate, the resulting solvent-sulfonate solution was washed three separate times with 2400 ml. of water for each washing. After each wash, 500 ml. of isopropyl alcohol was added to break the emulsion formed. After the third water wash, the solvent-sulfonate solution was heated to a bottoms temperature of 360° F. at an absolute pressure of 15 mm./Hg to remove the solvent. The resulting sulfonate contained 4.88% total barium, of which 4.7% was present as barium sulfonate.

EXAMPLE II

Preparation of basic barium sulfonate from a neutral barium sulfonate

100 grams of the product obtained from Example I hereinabove was heated to 320° F., after which there was added slowly a solution of 35 grams of barium hydroxide octahydrate (0.111 mol) in 75 ml. of water. The temperature decreased to 220° F. The temperature was slowly increased to 360° F. over a period of 3 hours, after which the mixture was heated to a final temperature of 360° F. at an absolute pressure of 30 mm./Hg. After the product had been filtered, it was analyzed and found to contain 10.02% total barium, of which 4.64%, by weight, was present as barium sulfonate, and 5.38% was found to be present as the basic barium.

The ratio of barium present as basic to that present as barium sulfonate was 1:16.

EXAMPLE III

Preparation of carbonated basic barium sulfonate

100 grams of the barium sulfonate prepared in Example I hereinabove was blended with 25 grams of a Gulf Coast Pale Oil having a viscosity of 300 SSU at 100° F. and heated to 300° F. A solution of 35 grams of barium hydroxide octahydrate in 35 ml. of water at 180° F. was slowly added to the sulfonate-oil solution. The temperature of the mixture dropped to 210° F., after which the temperature was increased to 225° F. to remove the water present, at which temperature carbon dioxide was slowly bubbled through the mixture. During the bubbling of the carbon dioxide, the temperature increased to about 300° F. The resulting composition was heated to a final bottoms temperature of 360° F. at an absolute pressure of 5 mm./Hg. After filtration, the product was found to contain 9.69% total barium, of which 3.42%, by weight, was present as barium sulfonate.

EXAMPLE IV

Preparation of carbonated basic barium sulfonates

50 lbs. of a lubricating oil concentrate of a basic barium petroleum sulfonate (1) was charged to a 15 gallon stainless steel reactor and heated to 300° F. Carbon dioxide gas was bubbled through the sulfonate for a period of 5 hours at 300° F. The resulting product was a bright amber colored liquid containing 12.1% of total barium (4.75% of which is present as a barium sulfonate; and 7.20% of which was present as basic barium).

The ratio of barium present as carbonated base to that present as sulfonate was 1.52.

(1) The oil concentrate of the basic barium sulfonate contained 12.48%, by weight, barium, of which 7.12% was basic barium and 4.8% was from the neutral barium sulfonate. The organic radical of the sulfonate was derived from a California solvent refined naphthenic base oil having a viscosity of 400 SSU at 100° F.

Table I hereinbelow presents data showing that the carbonated basic barium sulfonates of the prior art are ineffective as viscosity index improving agents.

TABLE I

Concentration of Carbonated Basic Barium Sulfonates (Weight percent)	Viscosity at 100° F. (SSU)	Viscosity at 210° F. (SSU)	Viscosity Index
None	144	42.4	89.2
5.0	159.5	43.4	88.9

EXAMPLE V

Preparation of a double carbonated, double basic barium sulfonate

A mixture of 100 grams of the same basic barium petroleum sulfonate described hereinabove in Example IV, containing 12.48%, by weight, of barium (4.80% of which was barium as a barium sulfonate, and 7.12% as basic barium) and 50 grams of a California naphthenic base oil having a viscosity of 300 SSU at 100° F. was heated to 300° F. To this mixture was slowly added 25 grams of $Ba(OH)_2.8H_2O$ (0.0794 mol) and 15 grams of urea (0.25 mol) in 75 grams of water previously heated to 160° F. A thick emulsion was formed. The temperature of the mixture was slowly increased to a maximum of 360° F. during a period of 4 hours, during which time a large amount of ammonia gas was evolved, leaving a hazy viscous amber colored liquid. An additional 49 grams of the base oil was blended therein as a diluent to reduce the viscosity of the composition. The mixture was heated to a liquid temperature of 360° F. at an absolute pressure of 5 mm./Hg. A stream of carbon dioxide gas was slowly bubbled through the resulting mixture at a temperature of 300° F. for a period of two hours. The mixture was filtered, and found to contain 8.25% by weight of barium and 0.38% by weight of nitrogen.

This product contained 2.4% by weight of barium as barium from the sulfonate. The ratio of total barium base as the barium sulfonate in the final product was 3.4.

Table II hereinbelow presents data showing the effectiveness of the carbonated basic barium sulfonate of Example V as a viscosity index improving agent.

TABLE II

Concentration of Carbonated Basic Barium Sulfonates (Weight percent)	Viscosity at 100° F. (SSU)	Viscosity at 210° F. (SSU)	Viscosity Index
None	206.5	46.86	97.8
5.00	429.0	81.00	144.2

EXAMPLE VI

Preparation of a double carbonated, double basic barium sulfonate

A mixture of 300 grams of the basic barium petroleum sulfonate described above for Example IV and 500 grams of a California paraffinic base oil having a viscosity of 150 SSU at 100° F. was heated to 300° F., to which was rapidly added an aqueous solution of 30.6 grams urea (0.510 mol) and 500 grams of $Ba(OH)_2.8H_2O$ (0.158 mol) in 150 grams of water. The temperature at this point dropped to 210° F. By increasing the temperature to 280° F. over a two-hour period, a greater proportion of the moisture present was removed. During this time, heavy ammonia gas evolution occurred.

Table III hereinbelow presents data obtained by the use of this additive as a viscosity index improving agent.

TABLE III

Concentration of the above Oil Solution of Double Carbonated, Double Basic Barium Sulfonates (Weight Percent)	Viscosity at 100° F. (SSU)	Viscosity at 210° F. (SSU)	Viscosity Index
None	144.0	42.4	89.2
4.0	161.2	44.7	115.3
6.0	170.6	46.2	121.2
8.0	182.0	47.6	126.1
10.0	193.3	49.1	132.2
12.0	205.9	50.9	135.0
15.0	224.2	53.5	139.4
18.0	245.5	56.3	141.6
21.0	268.8	59.7	144.3

EXAMPLE VII

Preparation of a double carbonated, double basic barium sulfonate

A mixture of 100 grams of the carbonated basic barium sulfonate prepared in Example IV hereinabove and 75 grams of a California naphthenic base oil having a viscosity of 300 SSU at 100° F., was heated to 220° F. A warm solution (about 170° F.) of 20 grams of barium hydroxide octahydrate (0.0635 mol) in 100 ml. of water was added at one time. The water was removed by agitating the mixture at 220° F. for a period of about 2 hours. The dehydration was completed by heating the mixture slowly to 360° F. at which time the mixture was thick. The mixture was cooled to 300° F. at which temperature a stream of carbon dioxide was slowly bubbled through the mixture for one hour. The resulting composition was an amber colored, viscous, bright liquid. After filtration, the product contained 7.53% basic barium and 2.54% barium as sulfonate barium.

The ratio of barium present as base to that present as a sulfonate was about 2.96.

When 6%, by weight, of the resulting product was dissolved in a petroleum oil, the viscosity index was increased from 89.2 to 147.2.

EXAMPLE VIII

Preparation of double carbonated, double basic barium sulfonate

A mixture of 1600 grams of the carbonated basic barium sulfonate prepared in Example IV hereinabove and 1200 grams of a paraffinic petroleum base oil having a viscosity of 200 SSU at 100° F. was heated to 176° F. A warm solution (180° F.) of 230 grams of barium hydroxide octahydrate (0.730 mol) in 500 ml. of water was added rapidly. The mixture was heated with constant agitation at about 220° F. for a period of about 20 hours for the purpose of removing the water. The temperature was then increased slowly to 300° F. during a period of 3 hours. Carbon dioxide gas was slowly added (bubbled in) for a period of 3 hours at 300° F. The resulting product was heated to 365° F. at an absolute pressure of 70 mm./Hg to remove all traces of moisture, then filtered. The filtered product contained a total of 9.8% barium, 2.6% of which was barium sulfonate, and 7.2% of which was basic barium. The ratio of basic

barium to sulfonate barium was 2.77. The finished product had the following physical characteristics:

Viscosity at 210° F. SSU	1,843
Viscosity at 100° F. SSU	7,707
Viscosity at 130° F. SSU	11,600
Viscosity index	125.2

Table IV hereinbelow presents data showing the effectiveness of this double carbonated, double basic barium sulfonate as a viscosity index improving agent in a California solvent refined paraffin base lubricating oil having a viscosity of 150 SSU at 100° F.

TABLE IV

Concentration of Carbonated Basic Barium Sulfonates (Weight percent)	Viscosity at 100° F. (SSU)	Viscosity at 210° F. (SSU)	Viscosity Index
None	143.4	42.36	89.2
5.0	219.2	54.9	146.3
7.0	258.8	60.60	148.2
9.0	299.5	69.2	152.0
12.0	378.6	87.1	152.9

Attempts were made to thicken oils and to improve the V.I. of oils by using the calcium counterpart of the double carbonated, double basic barium sulfonate of this invention. However, the calcium sulfonate did not thicken the oils or improve the viscosity index of the oils.

Oil compositions thickened with double corbonated, double basic barium sulfonates can be used as hydraulic oils, transmission fluids, etc.

I claim:

1. A lubricating oil composition comprising a major proportion of an oil of lubricating viscosity and from about 0.5% to about 25%, by weight, of a double carbonated, double basic barium sulfonate obtained by (1) reacting a neutral barium sulfonate with from 1 to 1.5 mols of barium hydroxide per mol of neutral barium sulfonate; (2) reacting the basic barium sulfonate of (1) at 250° F.–400° F. with from 0.5 to 1.0 mol of CO_2 per mol of basic barium content of the basic sulfonate of (1); (3) reacting the resulting carbonated basic barium sulfonate of (2) with from 1 to 1.5 mols of barium hydroxide per mol of neutral barium sulfonate of (1); and (4) reacting the product of (3) at 250° F.–400° F. with from 0.5 to 1 mol of CO_2 per mol of additional barium added in (3).

2. A lubricating oil composition comprising a major proportion of an oil of lubricating viscosity and from about 0.5% to about 25%, by weight, of a double carbonated, double basic barium sulfonate obtained by (1) reacting a neutral petroleum sulfonate with from 1 to 1.5 mols of barium hydroxide per mol of neutral petroleum sulfonate; (2) reacting the basic barium sulfonate of (1) at 250° F.–400° F. with from 0.5 to 1.0 mol of CO_2 per mol of basic barium content of the basic sulfonate of (1); (3) reacting the resulting carbonated basic barium sulfonate of (2) with from 1 to 1.5 mols of barium hydroxide per mol of neutral barium petroleum sulfonate of (1); and (4) reacting the product of (3) at 250° F.–400° F. with from 0.5 to 1 mol of CO_2 per mol of additional barium added in (3).

3. A lubricating oil composition comprising a major proportion of an oil of lubricating viscosity and from about 3% to about 8%, by weight, of a double carbonated, double basic barium sulfonate obtained by (1) reacting a neutral barium sulfonate with from 1 to 1.5 mols of barium hydroxide per mol of neutral barium sulfonate; (2) reacting the basic barium sulfonate product of (1) at 250° F.–400° F. with from 0.5 to 1.0 mol of CO_2 per mol of basic barium content of the basic sulfonate of (1); (3) reacting the resulting carbonated basic barium sulfonate of (2) with from 1 to 1.5 mols of barium hydroxide per mol of neutral barium sulfonate of (1); and (4) reacting the product of (3) at 250° F.–400° F. with from 0.5 to 1 mol of CO_2 per mol of additional barium added in (3).

4. A lubricating oil composition comprising a major proportion of an oil of lubricating viscosity, and from 0.5% to about 25%, by weight, of a double carbonated double basic barium sulfonate prepared by (1) reacting a neutral barium sulfonate of the formula:

$$[(R)_aASO_3]_2Ba$$

wherein R is a straight chain hydrocarbon radical having a molecular weight from about 150 to about 800, A is benzene, and a is a number from 1 to 4, with from 1 to 1.5 mols of barium hydroxide per mol of neutral sulfonate; (2) reacting the basic barium sulfonate of (1) at 250° F.–400° F. with from 0.5 to 1.0 mol of CO_2 per mol of basic barium content; (3) reacting the carbonated basic barium sulfonate of (2) with from 1 mol to 1.5 mols of barium hydroxide per mol of neutral barium sulfonate of (1); and (4) reacting the basic barium sulfonate of (3) at 250° F.–400° F. with from 0.5 to 1 mol of CO_2 per mol of barium hydroxide added in (3).

5. A lubricating oil composition comprising a major proportion of an oil of lubricating viscosity, and from 3% to about 8%, by weight, of a double carbonated double basic barium sulfonate prepared by (1) reacting a neutral barium sulfonate of the formula:

$$[(R)_aASO_3]_2Ba$$

wherein R is derived from a petroleum hydrocarbon radical having a molecular weight from about 150 to about 800, A is benzene, and a is a number from 1 to 4, with from 1 to 1.5 mols of barium hydroxide per mol of neutral sulfonate; (2) reacting at 250° F.–400° F. the basic barium sulfonate of (1) with from 0.5 to 1.0 mol of CO_2 per mol of basic barium content; and (3) reacting the carbonated basic barium sulfonate of (2) with from 1 mol to 1.5 mols of barium hydroxide per mol of neutral barium sulfonate of (1); and (4) reacting the basic barium sulfonate of (3) at 250° F.–400° F. with from 0.50 to 1 mol of CO_2 per mol of barium hydroxide added in (3).

References Cited in the file of this patent

UNITED STATES PATENTS

2,839,470	Warren et al.	June 17, 1958
2,881,206	Kjonaas et al.	Apr. 7, 1959