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PROCESS FOR CARBONATED METAL PHENATES

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This invention is directed to a new process for the preparation of metal salts of alkylated phenols. In particular, this invention pertains to a process for the preparation of carbonated metal salts of alkylated phenols.

Metal salts of phenols are used as additives for lubricants for internal combustion engines. Crankcase lubricants in internal combustion engines are exposed to extremely severe conditions of operation, particularly in diesel engine service, wherein the lubricating oil compositions encounter temperatures as high as 650° F. and higher, and pressures of 1,000 p.s.i. and higher. Under such operating conditions, the lubricating oil compositions have a tendency to deteriorate, forming gummy deposits on the piston rings, the piston lands, and the piston skirts. Such deposits cause ring sticking, markedly reducing the effectiveness of the top rings to seal off the products of the combustion chamber from the crankcase, etc. Thus, combustion products move past the piston rings into the crankcase oil, resulting in damage to the pistons and the cylinder walls, and a dilution and acidification of the lubricating oil. Furthermore, ring sticking caused by such deposits results in loss of power, high wear, ring breakage, general mechanical failures, etc.

Because of the greater use of high sulfur residual fuels in diesel engines, larger amounts of acidic products are formed, resulting in a need for particular additives described herein for the lubricating oil compositions. In view of their detergent and wear-reducing characteristics, metal phenates have been particularly effective as additives for heavy duty oils used for lubricating high speed diesel and gasoline engines. Metal phenates also inhibit wear and corrosive action on metal parts caused by corrosive products formed in internal combustion engines during stop and go city driving. More recently, the so-called basic metal phenates, that is, metal phenates containing more equivalents of metal than equivalents of alkylated phenol, have become of greater importance for use as additives in lubricating oil compositions than the normal metal phenates which contain equal or less equivalent amounts of metal than alkylated phenol. Thus, basic metal phenates are useful not only as detergents and wear inhibitors, but also as acid neutralizers in lubricating oil compositions.

Numerous processes have been contemplated for the preparation of metal alkyl phenates, in particular metal alkyl phenates capable of imparting high basicity to lubricating oil compositions. The prior processes are time-consuming and costly. For example, processes have been described wherein certain dihydric alcohols such as ethylene glycol are used as reaction media for the formation of basic salts of phenols. However, such processes, because of the use of high boiling alcohols which require high temperatures and vacuum mechanisms for their removal, make the processes time-consuming and costly. Furthermore, in the so-called carbide process for the preparation of metal salts of alkyl phenols, the high temperatures result in the formation of salts which are dark in color, imparting an unfavorable color to the oil blend.

It is, therefore, an object of this invention to set forth a process for the preparation of metal alkyl phenates, particularly metal phenates of high basicity, which phenates are compatible with other lubricating oil addition agents, forming lubricating oil compositions useful for heavy duty diesel engine service.

In accordance with this invention, it has been discovered that basic carbonated metal alkyl phenates can be prepared by reacting an alkylated phenol with an alkaline earth metal hydroxide or oxide in the presence of urea.

The carbonated basic metal phenates obtained by the process of this invention are particularly effective as detergents and corrosion inhibitors in oils which require unusually large amounts of acidic neutralization.

The process of this invention is particularly suitable for the formation of basic carbonated metal salts of oil-soluble alkylated phenols containing from 1 to 5, particularly from 1 to 3, straight-chain, branched-chain, or cyclic, saturated or unsaturated, hydrocarbon radicals attached to the benzene ring, each radical having up to 30 carbon atoms, more preferably from 4 to 30 carbon atoms. Examples of suitable hydrocarbon radicals include alkyl radicals such as butyl, hexyl, octyl, decyl, dodecyl, hexadecyl, eicosyl, triacontyl radicals; radicals derived from petroleum hydrocarbons such as white oil, wax, olefin polymers (e.g., polypropylene and polybutene), etc.; cyclic non-benzenoid radicals, such as cyclohexyl, bornyl, etc.; alkoxy radicals such as pentoxy, octoxy and cetoxy radicals, etc.

Examples of alkylated phenols include: dodecyl phenol, tetradecyl phenol, octadecyl phenol, hexadecyl phenol, dibutyl phenol, dioctyl phenol, dihexadecyl phenol, dioctadecyl phenol, tributyl phenol, trioctadecyl phenol, eicosyl phenol, triacontyl phenol, alkyl phenols wherein the alkyl groups are derived from alkylene polymers, pentoxy phenol, octoxy phenol, meta-, ortho- and paracetoxy phenols, etc.

The metal hydroxides and oxides include the hydroxides and oxides of alkaline earth metals (i.e., calcium, barium, and strontium), and magnesium.

In certain instances, it may be desirable to substitute thiourea or methylurea for all or a part of the urea.

Briefly, in the preparation of basic carbonated phenates according to the process described herein, an alkyl phenol is reacted with a metal hydroxide or oxide in the presence of urea. Also, if so desired, a carbonated basic metal alkyl phenate can be prepared by reacting a normal or slightly basic metal phenate with a metal hydroxide or oxide in the presence of urea.

In the preparation of carbonated basic metal alkyl phenates from normal metal phenates, the metal hydroxide or oxide is used in amounts of 0.25 mol to 1.5 mol per mol of normal metal phenate. In the preparation of a carbonated basic metal phenate from an alkyl phenol, the metal hydroxide or oxide is used in amounts of 1 mol to 2 mols per mol of phenol. It is preferred that the mol ratio of metal hydroxide to the normal phenate be at least 0.75 to 1.5, that is, that there be present from 0.75 to 1.5 mols metal in excess of that necessary for the formation of a normal phenate.

In the preparation of carbonated basic metal phenates, the amount of metal hydroxide or oxide used will depend on the amount of basicity desired in the final metal phenate; however, the preferable limitations are to use at least 0.75 mol to as high as 1.5 mols of metal hydroxide or oxide per mol of normal phenate.

Similarly, with regard to the urea, it is desirable to use at least 0.1 mol of urea per equivalent of metal content used in the metal hydroxide or oxide, with a preferred range of 0.5 mol to 1 mol of urea per equivalent of metal hydroxide or oxide used.

The lubricating oils which are improved by the carbonated basic metal phenates prepared by the described process, which oils can also serve as reaction media, include a

wide variety of oils, such as mineral oils, exemplified by naphthenic base, paraffin base, and mixed base oils derived from petroleum; synthetic oils, such as alkylene polymers, including polymers of propylene; polymers of alkylene oxides and esters of dicarboxylic acids; polymers of silicon; aromatic type oils, such as alkyl benzenes, alkylphenyl diethers, alkyl biphenyls, and polyphenyls, etc.

In the formation of lubricating oil compositions according to the described process, the lubricating oil compositions contain the carbonated basic metal phenates prepared by the described process in amounts sufficient to inhibit piston groove deposit formation; and control ring and cylinder wear by neutralizing corrosive acids, which amounts may be from 0.25%, by weight, to 50%, by weight, with 2%, by weight, to 20%, by weight, being preferred.

In general, this new process comprises blending an alkyl phenol, a lubricating oil, an alkaline earth metal hydroxide or oxide, and urea at temperatures ranging from 70° F. to 200° F., and heating the blend at temperatures ranging from 200° F. to 400° F. for a time sufficient to decompose the urea and form the desired carbonated metal alkyl phenate, followed by filtration.

If so desired, methyl urea may be used to replace all or a part of the urea.

The following examples illustrate the formation of carbonated basic metal phenates in accordance with this invention.

Example I.—Preparation of Carbonated Basic Calcium Alkyl Phenate

In an atmosphere of nitrogen, a mixture of 446 grams of an alkyl phenol (1.3 mols) wherein the alkyl radical was derived from a polypropylene having an average of 12–14 carbon atoms, and 81 grams of calcium oxide was blended at 175° F., then heated to 190° F., after which an aqueous solution of urea (60 grams of urea in 48 grams of water) was added. To this mixture was added 600 grams of a California base oil having a viscosity of 145 SSU at 100° F. The whole mixture was heated gradually to 350° F. at atmospheric pressure, and agitated at that temperature for 22 hours.

The resulting solution was cooled to 190° F., and 52 grams of calcium oxide was added, followed by the addition of a solution of 40 grams of urea in 32 grams of water. The mixture was agitated continually for a period of 44 hours at 350° F. The reaction mixture was then filtered to separate insoluble residues and unreacted calcium hydroxide. The filtrate had a calcium content of 4.44%, by weight, and 2.7% CO_2. This product was soluble in paraffinic, naphthenic, and mixed base mineral oils in all proportions.

Example II.—Preparation of Carbonated Basic Barium Alkyl Phenate

In a nitrogen atmosphere, a mixture of 375 grams of an alkyl phenol (1.1 mols), wherein the alkyl radical was derived from a polypropylene containing an average of 12–14 carbon atoms, 208 grams of barium oxide, and 170 grams of a California base oil having a viscosity of 145 SSU at 100° F., was agitated at 190° F. at atmospheric pressure. 336 grams of the same base oil was added, after which an aqueous solution of 51 grams of urea in 41 grams of water was added slowly at temperatures from 200° F. to 240° F. with cooling. The whole mixture was agitated for a period of 22 hours at 350° F. The reaction mixture was filtered to remove insoluble residue material and unreacted barium oxide. The resulting product had a barium content of 15.4%, by weight, and 2.3% CO_2.

Example III.—Preparation of Carbonated Basic Calcium Alkyl Phenate

A mixture of 232 grams of the same alkyl phenol described hereinabove, 35 grams of powdered calcium hydroxide (0.472 mol) and 218 grams of California base oil having a viscosity of 100 SSU at 100° F. was agitated at 280° F. to form a uniform mixture. Granular urea, in an amount of 21 grams (0.346 mol) was added over a period of 4 hours in small increments. During that 4-hour period the temperature was slowly increased to 400° F., at which time a second amount of calcium hydroxide in an amount of 35 grams was added, while the portionwise addition of urea was continued until 21 grams of urea had been added over an additional 2-hour period. The temperature was held in the range of 380° F. to 400° F. during all this time. After filtration, the product contained 3.60%, by weight, of calcium.

Example IV.—Preparation of Carbonated Basic Barium Phenate

A mixture of 232 grams of the same alkyl phenol described hereinabove (0.663 mol) and 218 grams of a California base oil having a viscosity of 100 SSU at 100° F. was agitated at 300° F. until there was a thorough blending of the components. Barium hydroxide octahydrate was added in small proportions over a period of 1 hour in an amount of 104.4 grams (0.331 mol) at a temperature in the range of 270° F. to 300° F. A mixture of 104.4 grams of barium hydroxide octahydrate and 21.8 grams of urea (0.363 mol) was then slowly added during a period of 1 hour, with the temperature being maintained in the range of 270° F. to 300° F. The mixture was then blown with nitrogen for a 2-hour period at temperatures ranging from 300° F. to 340° F., followed by filtration. The filter product was a dark colored fluid which was oil soluble in all proportions and having 13.5%, by weight, of barium.

Example V.—Preparation of Carbonated Basic Calcium Phenate

A mixture of 262 grams of the same alkyl phenol described hereinabove, 197 grams of a California base oil having a viscosity of 150 SSU at 100° F., 24.8 grams of urea, and 46.2 grams of calcium oxide was agitated for a period of 5 hours at 338° F., after which nitrogen gas was blown through the reaction mixture at the same temperature for 1 hour. The filtered reaction mixture contained 3.9% by weight of calcium.

Example VI.—Preparation of Carbonated Basic Calcium Phenate

A mixture of 262 grams of the same alkyl phenol described hereinabove, 197 grams of a California base oil having a viscosity of 150 SSU at 100° F., 49.6 grams of urea and 46.2 grams of calcium oxide was agitated for a period of 5 hours at 338° F., followed by nitrogen blowing for 1 hour at the same temperature. The reaction mixture was filtered, and the filter product contained 3.0% calcium, by weight.

Example VII.—Preparation of Sulfurized Calcium Alkyl Phenate

A mixture of 350 grams of the alkyl phenol identified hereinabove, 74 grams of calcium hydroxide, 16 grams of sulfur, 60 grams of urea, and 100 grams of a California base oil having a viscosity of 200 SSU at 100° F. was slowly heated with agitation to 370° F., during which time a stream of nitrogen gas was passed through the reaction vessel. The mixture was heated at 370° F. for 1.25 hours, after which the product was filtered. The filtrate contained 3.30%, by weight, calcium and 1.44% sulfur.

Example VIII hereinbelow illustrates the use of methyl urea as a reactant, replacing urea.

Example VIII.—Preparation of Normal Calcium Alkyl Phenate by Means of Methyl Urea

A mixture of 116 grams of the same alkyl phenol described hereinabove, 109 grams of a California base oil

having a viscosity of 100 SSU at 100° F., 35 grams of calcium hydroxide, and 21.9 grams of methyl urea was agitated for a period of 6½ hours at temperatures ranging from 203° F. to 338° F. The filtered reaction product contained 5.17% calcium, by weight.

We claim:

1. A process of preparing basic carbonated alkaline earth metal alkylated phenates consisting essentially of reacting an alkyl phenol wherein said alkyl radical is derived from a polypropylene having an average of 12–14 carbon atoms, with an alkaline earth metal hydroxide with urea present in the reaction mixture at temperatures ranging from 70° F. to 200° F., wherein said alkaline earth metal hydroxide is present in an amount such that there are from 0.75 mol to 1.5 mols of alkaline earth metal hydroxides in excess of that necessary for the formation of a normal phenate, wherein said urea is present in an amount of from 0.5 mol to 1 mol per equivalent of alkaline earth metal hydroxide.

2. A process of preparing basic carbonated alkaline earth metal alkylated phenates consisting essentially of reacting an alkyl phenol wherein said alkyl radical contains from 4–30 carbon atoms, with an alkaline earth metal hydroxide with urea present in the reaction mixture at temperatures ranging from 70° F. to 200° F., wherein said alkaline earth metal hydroxide is present in an amount such that there are from 0.75 mol to 1.5 mols of alkaline earth metal hydroxides in excess of that necessary for the formation of a normal phenate, wherein said urea is present in an amount of from 0.5 mol to 1 mol per equivalent of alkaline earth metal hydroxide.

3. A process of preparing basic carbonated calcium alkylated phenates consisting essentially of reacting an alkyl phenol wherein said alkyl radical is derived from a polypropylene having an average of 12–14 carbon atoms, with calcium hydroxide with urea present in the reaction mixture at temperatures ranging from 70° F. to 200° F., wherein said calcium hydroxide is present in an amount such that there are from 0.75 mol to 1.5 mols of calcium hydroxide in excess of that necessary for the formation of a normal phenate, wherein said urea is present in an amount of from 0.5 mol to 1 mol per equivalent of calcium hydroxide.

4. A process of preparing basic carbonated barium alkylated phenates consisting essentially of reacting an alkyl phenol wherein said alkyl radical is derived from a polypropylene having an average of 12–14 carbon atoms, with barium hydroxide, with urea present in the reaction mixture, at temperatures ranging from 70° F. to 200° F., wherein said barium hydroxide is present in an amount such that there are from 0.75 mol to 1.5 mols of barium in excess of that necessary for the formation of a normal phenate, wherein said urea is present in an amount of from 0.5 mol to 1 mol per equivalent of barium hydroxide.

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