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(54) Process for preparing overbased phenates.

(57) Overbased sulfurized alkaline earth metal alkylphenate having excellent water tolerance properties in lubricant formulations is prepared by charging into a reactor a preheated (280-380 °F) mixture of alkaline earth metal base and alkylphenol (preferably in oil), while simultaneously, but separately, charging a promoter solvent such as a glycol. Then a controlled amount of molten sulfur is charged at a rate that controls the reaction exotherm and off-gas evolution, while maintaining the 280-380 °F temperature. Upon completing the sulfur charge, the reactor contents are allowed to interact at 280-380 °F long enough to form the sulfurized alkylphenate. While keeping the temperature at 280-380 °F, the sulfurized alkylphenate is overbased by charging the reactor simultaneously with controlled amounts of alkaline earth metal base, promoter solvent, and carbon dioxide gas, at a controlled charge rate not much greater or less than the rate at which the reactants undergo reaction to form the overbased phenate. Upon completing the charging of the alkaline earth metal base and promoter solvent, the carbon dioxide charge is continued until completion of the carbonation reaction. Unreacted alkylphenol and promoter solvent are stripped off under vacuum with inert gas purge at 400-480 °F, and the resultant reaction product is filtered and the filtered product recovered. The reaction cycle time is no more than about 6 hours, and the filtered product has water tolerance properties normally associated with a batch preparation of the same product requiring a reaction cycle time of at least 8 hours.

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Background of the Invention

1. Field of the Invention

The present invention relates generally to processes for manufacturing overbased sulfurized alkaline earth metal alkylphenates in which an alkaline earth metal base, sulfur, and an alkylphenol are first reacted in the presence of a mutual solvent to form a sulfurized metal phenate intermediate, following which the intermediate is overbased via carbonation in the presence of additional alkaline earth metal base. In particular, the invention concerns a batch process in which throughput is substantially increased by conducting the carbonation step in a single stage in which CO_2 is introduced to the reaction vessel concurrently with the introduction of alkaline earth metal base at a prescribed mole ratio of CO_2 to metal base.

2. Discussion of Background Art

Lubricating oils tend to deteriorate under normal conditions encountered in present day diesel and automotive engines. Sludge, lacquer and resinous materials can form and adhere to engine parts, especially piston rings, grooves and skirts which can have a harmful effect on engine efficiency, operation and useful life. Commonly, additives are incorporated in lubricating oils to reduce the formation of such materials or to keep them suspended so that engine parts are kept clean and operating properly. Additives which reduce the tendency of lubricating oils to form oxidation products are called antioxidants, while additives which tend to suspend oxidation products and sludges, or cleanse the engine parts of such products, are called detergents or dispersants. It is not uncommon for certain additives to exhibit both antioxidant and detergency properties.

Overbased sulfurized alkaline earth metal alkylphenates have been found to be especially useful for the dual purpose of providing oxidation inhibition and detergency in a lubricating oil.

The term "overbased" refers to the fact that the phenate material incorporates a large excess of alkaline earth metal base over that necessary to neutralize the phenate. Typically, an overbased phenate will have a TBN (total base number) of about 100-400. Such high basicity, which enables the additive to neutralize harmful acids formed in engine combustion, is accomplished using a well known technique usually referred to as carbonation or carbonate overbasing. This technique generally involves formation of an initial alkaline earth metal sulfurized phenate intermediate having relatively low levels of metal base. This intermediate is then treated with a large excess of additional alkaline earth metal. In a reaction that is not well understood, the sulfurized metal phenate intermediate is reacted with the excess metal base in a suitable solvent, usually a glycol, by subjecting the reactants to blowing with gaseous carbon dioxide. The CO_2 treatment, or carbonation, results in the formation of a fine colloidal dispersion whereby the excess metal base is essentially "dissolved."

It is well known in the art to carry out the manufacture of overbased sulfurized alkaline earth metal alkylphenates in either a batch process or a continuous process. There are significant advantages and disadvantages attendant to both types of processing.

For example, batch processing has the major disadvantage that, as would be expected, much less product can be manufactured over a given period of time than would be the case if one used a continuous process. Nevertheless, a very significant advantage in batch processing is that the degree or extent of carbonation can be very closely and reliably controlled. This is important because overcarbonating or undercarbonating the overbased phenate can result in serious problems. Overcarbonated product generally shows poor water tolerance in lubricant formulations and is hazy due to break up of the colloidal dispersion mentioned above. Undercarbonated product tends to have increased viscosity, poor filterability, and resists glycol stripping. Batch processing avoids these problems and, in particular, is the method of choice if a water tolerant phenate is a critical objective.

Continuous processing has the advantage of maximizing production throughput. However, in continuous processes typically a first reactor is used to carry out formation of the initial sulfurized metal phenate intermediate while a second reactor or a series of successive reactors are used for carbonation. A well-known phenomenon associated with continuous processes is that of residence time distribution. This phenomenon is particularly detrimental in the carbonation step of continuous phenate processes because it results in the formation of both overcarbonated and undercarbonated phenate. For this reason, overbased phenates prepared in continuous processes generally elicit significantly poorer water tolerance than batch prepared phenates. The residence time distribution phenomenon can be minimized by increasing the number of reactors used for the carbonation step to approximate a plug flow reactor, but not without

substantial capital outlay.

Ideally, it is desired to have the best of both worlds--the production throughput of continuous processing, with the control over carbonation afforded by batch processing, to ensure a phenate having excellent water tolerance properties.

There are numerous patents directed to the manufacture of overbased sulfurized alkaline earth metal alkylphenates. Belgium Patent No. 876,119, thought to be the most pertinent, discloses a process for manufacturing a sulfurized overbased alkaline earth metal alkylphenate in which formation of a sulfurized metal phenate intermediate is achieved by contacting a Group II metal base, alkylphenol, and a mutual solvent in a heat exchanger for a time sufficient to form a metal phenate and then passing the phenate without substantial cooling into a reaction zone where said metal phenate is contacted at reaction conditions with sulfur to form the sulfurized metal phenate. This intermediate can then undergo carbonation with CO_2. Although the patent refers to "semi batch" processes where reactants are added to a reaction vessel while reaction is occurring, the patent fails to teach or suggest the unique measures adopted in the present invention with respect to carbonation.

A general object of the present invention is to provide a batch process for preparing overbased metal phenate having improved production throughout without at the same time incurring the disadvantages associated with continuous processing. Other objects will be apparent herein-after to those skilled in the art.

Summary of the Invention

The present invention is a process for preparing an overbased sulfurized alkaline earth metal alkylphenate which comprises the steps of: (a) contacting at reaction conditions in a reaction vessel a mixture comprising an alkylphenol, sulfur, a promoter solvent, and an alkaline earth metal base to form a sulfurized alkaline earth metal alkylphenate; followed by (b) overbasing the sulfurized alkaline earth metal alkylphenate formed in (a) above by charging simultaneously to said reaction zone and reacting therein under reaction conditions (i) alkaline earth metal base (ii) promoter solvent and (iii) carbon dioxide at a mole ratio of carbon dioxide to alkaline earth metal base of about 0.40:1 to about .95:1 and at a controlled rate not substantially greater or less than the rate at which the carbon dioxide, alkaline earth metal base, and sulfurized alkaline earth metal phenate undergo reaction; and (c) upon completion of said charging of alkaline earth metal compound and promoter solvent to the reaction zone, allowing said carbon dioxide charge to continue until completion of the reaction.

In a related embodiment the invention is further directed to a process for preparing an overbased sulfurized alkaline earth metal alkylphenate which comprises the steps of: (a) passing a mixture consisting essentially of alkaline earth metal base and alkylphenol in a mole ratio of about 0.1:1 to about 1.0:1 through pre-heating means into a reaction vessel such that said mixture enters the reaction vessel pre-heated to a temperature of from about 280° to 380°F; while simultaneously charging about 0.1 to about 1.0 moles of a promoter solvent per mole of alkylphenol into the reaction vessel; followed by (b) charging into the reaction vessel about 1.0 to about 2.0 moles of sulfur per mole of alkylphenol over a period of about 20-180 minutes, while maintaining the reaction vessel at a reaction temperature of about 280-380°F; (c) upon completion of the sulfur charge, allowing the contents of the reaction vessel to interact at said reaction temperature for a period of time sufficient to form a sulfurized alkaline earth metal alkylphenate; (d) converting the sulfurized alkaline earth metal alkylphenate formed above to an overbased phenate by charging simultaneously to said reaction vessel and reacting therein at a temperature of from about 280° to about 380°F, (i) about 0.5 to 2.0 moles alkaline earth metal base per mole of alkylphenol, (ii) about 0.5 to 2.0 moles of promoter solvent per mole of alkylphenol; and (iii) about .40 to about .95 moles of carbon dioxide gas per mole of alkaline earth metal base, at a controlled charge rate not substantially greater or less than the rate at which the reactants present in the vessel undergo reaction to form the overbased phenate; and (e) upon completion of said charging of alkaline earth metal base and promoter solvent to the reaction vessel, allowing said carbon dioxide charge to continue until completion of the reaction.

While the present invention may be considered a batch process, the method of carbonation used in the process significantly reduces the reaction cycle time so that the process can approach or equal the production throughput of a continuous process. A further reduction in reaction cycle time can be achieved if, as required in the above related embodiment, the sulfurization step utilizes a preheating means to introduce the alkylphenol and metal base into the reaction vessel at the temperature of reaction as opposed to charging them at ambient temperature and waiting for the reactor to heat up to the desired reaction temperature. Overbased phenates prepared using the process of the present invention elicit excellent water tolerance properties usually associated with batch processing even though the process can reduce the reaction cycle time of a typical 9 to 10 hour batch reaction by as much as 4 to 5 hours.

Detailed Description

Generally speaking, the process of the present invention can be carried out in a single commercial size stirred tank reactor in two stages. In the first stage, a sulfurized alkaline earth metal alkylphenate intermediate is formed by contacting under reaction conditions a suitable alkylphenate, an alkaline earth metal base, and sulfur in the presence of a promoter or mutual solvent. In the second stage of the process (carbonation) the sulfurized metal phenate intermediate undergoes treatment with CO_2 gas in the presence of an additional amount of alkaline earth metal base and promoter solvent. By effecting certain modifications to one or both of these stages, the present invention dramatically reduces the reaction cycle time required to produce a furnished batch of overbased phenate product. Each of the two stages will now be discussed in greater detail.

Formation of Sulfurized Metal

Phenate Intermediate

In the front end of the process of the present invention an alkylphenol, an alkaline earth metal base and sulfur are reacted in the presence of a promoter solvent to form a sulfurized metal phenate.

The alkylphenols useful in the present invention are of the formula $R(C_6H_4)OH$ where R is a straight chain or branched chain alkyl group having from 8 to 40 carbon atoms and preferably from 10 to 30 carbons, and the moiety (C_6H_4) is a benzene ring. Examples of suitable alkyl groups are octyl, decyl, dodecyl, tetradecyl, hexadecyl, etc.

The alkaline earth metal base can be a base of calcium, barium, magnesium and strontium. Preferred are calcium and magnesium. The most commonly used bases are the oxides and hydroxides of the above metals such as calcium oxide, calcium hydroxide, barium oxide, barium hydroxide, magnesium oxide, and the like. Calcium hydroxide, commonly called hydrated lime, is most commonly used in the manufacture of sulfurized calcium phenates, and it is preferred to use hydrated lime of good quality (relatively free of carbonates) which has not deteriorated during storage.

The promoter solvent, also sometimes referred to as a mutual solvent, can be any stable organic liquid which has appreciable solubility for both the alkaline earth metal base, the alkylphenol, and the sulfurized metal phenate intermediate. Although a wide variety of mutual solvents are known in the art, many of such suitable solvents are glycols and glycol monoethers such as ethylene glycol, 1,4-butane diol, derivatives of ethylene glycol, such as monomethyl ether, monoethyl ether, etc. The vicinal glycols are preferred and ethylene glycol is most preferred because it serves to activate the neutralization reaction and to that extent typifies a catalyst, although the exact characteristics describing its function are unknown.

The sulfur used in the reaction is elemental sulfur. In the present invention it has been found desirable to use molten sulfur.

It is further desirable, although not required, in the present invention to use as a promoter in formation of the sulfurized phenate a low base alkylbenzene sulfonate. The sulfonates suitable for use are, e.g., the sulfonic acid salts of molecular weight preferably of more than 400 obtained by sulfonating alkyl-benzenes derived from olefins or polymers of C_2 to C_4 olefins of chain length C_{15}-C_{80} and alkaline earth metals such as calcium, barium, magnesium etc. In the Examples following this discussion, a low base calcium sulfonate prepared from a polypropene of about C-60 chain length was included in the sulfurization reaction.

In addition to the above reactants, formation of the sulfurized metal phenate is desirably carried out in the presence of a lubricating oil reaction diluent. The lubricating oil can be any lubricating oil that is used in the final lubricating oil formulation containing the phenate prepared by the present invention such as a 5W, 10W or 40W oil, including naphthenic base, paraffin base and mixed based mineral oils. A 5W oil is generally most suitable as a reaction diluent.

The range of reaction stoichiometry for the above reactants is as follows:

	Range	Preferred Range
Sulfur, mol/mol DDP*	1.0-2.0	1.3-1.6
$Ca(OH)_2$, mol/mol DDP	0.1-1.0	0.4-0.6
Glycol, mol/mol DDP	0.1-1.0	0.4-0.6

*dodecylphenol

The amount of diluent oil is generally about 200 to 300 grams per mole of alkylphenol. The amount of low base sulfonate (if used) is about 10-20 grams per mole of alkylphenol.

The reaction to form the sulfurized alkaline earth metal alkylphenate is carried out in the present invention by contacting the alkaline earth metal base, the alkylphenate, the promoter solvent, the lubricating oil diluent, and the optional low base sulfonate at a reaction temperature of about 280° to about 380°F, preferably about 320° to about 360°F for sufficient time to form the desired intermediate, normally about 40 to 80 minutes.

To avoid the time wasted while the reactor is being raised to the desired reaction temperature of 280°-380°F, the alkylphenol and alkaline earth metal base are preferably charged to the reactor across a preheater set at the desired reaction temperature while simultaneously the promoter solvent is charged to the reaction vessel separately. It is preferred not to charge the glycol solvent across the preheater with the $Ca(OH)_2$ and alkylphenol because the glycol will form a complex (calcium glycol oxide) which will plug up the preheater, typically a heat exchanger.

After the metal base, alkylphenol and promoter solvent have been added, the sulfur is added to the reaction mixture at a sufficiently slow rate to control the reaction exotherm and off-gas evolution. Slow sulfur addition (over a period of 30-60 minutes) is particularly important if the alkylphenate and metal base have been charged to the reaction vessel preheated.

Carbonation

Following formation of the sulfurized metal phenate intermediate as described above, carbonate overbasing can be achieved according to the present invention by adding more alkaline earth metal base and promoter solvent to the reaction vessel while simultaneously carbonating with CO_2 gas. The range of reaction stoichiometry for the carbonation is as follows:

	Range	Preferred Range
$Ca(OH)_2$, mol/mol DDP*	0.5-2.0	1.0-1.5
Glycol, mol/mol DDP	0.5-2.0	1.0-1.5
CO_2, mol/mol DDP	0.5-2.0	1.0-1.5

*Dodecylphenol

In accordance with the present invention, the alkaline earth metal base, promoter solvent, and CO_2 are charged to the reaction vessel simultaneously at a mole ratio of CO_2 to alkaline earth metal base of about .40:1 to about .95:1 and at a controlled rate such that the rate of charging the reactants is not substantially greater or less than the rate at which the carbonation reaction can proceed. If the rate is substantially faster than the speed at which the carbonation can occur the reaction mixture will become very viscous it will be difficult to conduct the carbonation due to formation of glycol oxide complexes, and the resulting product will generally be poorer in quality. If the rate of charging is substantially slower than the rate at which the carbonation reaction can occur the reaction cycle time is unnecessarily prolonged.

As an example, in the case of a commercial 3000 gallon stirred tank reactor, it has been determined that a suitable rate for charging of the alkaline earth metal (in the form of a 480 TBN $Ca(OH)_2$ slurry in 5W oil) is about 70-90 lbs per minute; a suitable rate for the glycol charge is about 10-15 lbs per minute and a suitable CO_2 charge rate is about 7000 SCFH.

The mole ratio at which the CO_2 and alkaline earth metal base are charged to the reaction vessel during the carbonation step constitutes a critical feature of the present invention. If the mole ratio of CO_2 to metal base being charged is below about .40 the reaction mixture will become too viscous and difficult to process, and the resultant product will have poor quality as evidenced by water intolerance. At mole ratios greater than .95 there is a danger of forming overcarbonated product which will result in a hazy phenate product also characterized by poor water tolerance properties. A preferred charge ratio of CO_2 to alkaline earth metal is about .75 to .85:1.

The carbonation reaction can be conducted in the temperature range of about 300° to about 360°F and preferably from about 330° to about 350°F. Preferably, the alkaline earth metal base (in 5W oil) is charged to the reaction across a preheater set at the desired reaction temperature for the carbonation.

After the alkaline earth metal base and glycol have been completely charged to the reaction vessel, the CO_2 charge is allowed to continue until the carbonation reaction is complete. Completion is evidenced by off-gas "breakthrough" i.e., a sharp increase in the reactor off gas when the charged CO_2 is no longer being

absorbed into the reaction medium. Generally, completion is deemed to occur 5 minutes after the reactor off-gas exceeds 5000 SCFH.

Following carbonation, the overbased product can be stripped to remove unreacted glycol and alkylphenol. This is typically done under vacuum with a nitrogen purge at 400° to 480°F. After stripping the product is filtered to remove fine solids.

The overbased sulfurized phenates prepared according to the present invention are suitable as detergent/antioxidant additives for lubricating oils, particularly those used in marine diesel engines.

EXAMPLE I

(Comparative)

In this example an overbased sulfurized alkaline earth metal alkylphenate is prepared using a batch method. Eighty gallons of 5W oil were charged into a commercial 3000 gallon stirred tank reactor. Into the reactor was then charged 7300 lbs of a 180 TBN calcium hydroxide dodecylphenol slurry. This slurry was previously prepared by combining 1700 gallon of dodecylphenol containing about 5.0 wt.% of an alkaline earth metal sulfonate with 1740 lbs of $Ca(OH)_2$ and 1 quart of a commercially obtainable silicone antifoamant, to result in a slurry having a TBN (total base number by ASTM D-2896) of 180. Simultaneously with the charging of dodecylphenol calcium hydroxide slurry to the reactor, 7128 lbs of ethylene glycol were charged into the reactor. The reactor was then brought to a temperature of 250°F at which point 1150 lbs of molten sulfur were charged to the reactor. The reactor was then brought to a temperature of 330°F and held there for 60 minutes to accomplish formation of the sulfurized calcium phenate. A first stage of carbonate overbasing was then undertaken by charging 3260 lbs of a 480 TBN slurry of calcium hydroxide in 5W oil and 510 lbs of ethylene glycol to the reactor. The 480 TBN slurry of calcium hydroxide in 5W oil was previously prepared by mixing 1240 gallons of 5W, 1 quart of antifoam, and 4140 lbs of $Ca(OH)_2$ in a suitable holding tank. Following the charge of the 480 TBN slurry and additional glycol the entire reaction mixture was nitrogen stripped with 2000 SCFH N_2. After nitrogen stripping the reaction mixture was carbonated with 7000 SCFH CO_2 until completion of the carbonation as indicated by a sharp increase in the reactor off-gas. Upon completion of the first carbonation stage a second carbonation stage was undertaken by introducing a second charge (3260 lbs) of the 480 TBN calcium hydroxide/5W oil slurry and ethylene glycol (510 lbs) into the reactor, followed by nitrogen stripping. The reaction mixture was again carbonated with 7000 SCFH CO_2 until completion of the carbonation as evidenced by a sharp increase in off-gas breakthrough. The reaction product was then stripped in a conventional manner to remove unreacted glycol and alkyphenol and then filtered to remove solid particles. The final product had the following inspection: calcium (wt.%) 9.4; sulfur (wt.%) 3.0; glycol (wt.%) 0.1; carbonate C (wt.%) 1.7; TBN (mg. KOH/g) 267; PM Flash (°F) 356; viscosity (cSt at 100°C) 151; BS&W (Vol. %) 0.02.

EXAMPLE II

(Comparative)

In this example sulfurized overbased calcium phenate was prepared in a continuous process utilizing two 3000 gallon reactors in series. To the first reactor controlled at 350°F were charged 32 lbs per minute of a 270 TBN calcium hydroxide dodecylphenol slurry, 3.4 lbs per minute of ethylene glycol and 4.9 lbs per minute of sulfur. To the second reactor, also controlled at 350°F, were charged reactor effluent from the first reactor via level control, 46 lbs per minute of a 330 TBN calcium hydroxide dodecylphenol slurry, 9.6 lbs per minute of ethylene glycol, and 2300 SCFH CO_2. Effluent from the second reactor was continuously transferred via level control for stripping and filtration. The final product had the following inspection: Calcium (wt.%) 9.4; Sulfur (wt.%) 3.2; Glycol (wt.%) 0.1; Carbonate C (wt.%) 1.3; TBN (Mg KOH/g) 254; PM Flash (°F) 350; Viscosity (cSt at 100°C) 275; BS&W (Vol.%) <0.05.

EXAMPLE III

In this example an overbased sulfurized calcium dodecylphenate was prepared in accordance with the present invention. Into a commercial 3000 gallon stirred tank reactor was charged 80 gallons of 5W oil. Seven thousand three hundred lbs of a 180 TBN calcium hydroxide dodecylphenol slurry (refer to the slurry preparation in Example I, above) was charged into the reactor through a preheater set at 330°F in order to raise the temperature of the slurry to 330°F just prior to its introduction to the reaction vessel. At the same

time, but separately, 728 lbs of ethylene glycol were charged into the reactor. Molten sulfur was then charged to the reaction vessel at rate of 29 lbs per minute until a total of 1150 lbs were charged. Following the 180 TBN slurry charge, 50 gallons of 5W oil were added to the reactor through the same line used to charge the slurry. The reaction mixture was then held for thirty minutes at 330 °F to accomplish formation of the sulfurized calcium dodecylphenate intermediate. Carbonation of the intermediate was then carried out by charging a 480 TBN calcium hydroxide/5W oil slurry (see Example I for slurry preparation) to the reaction vessel across a second preheater set at 330 °F and a charge rate of 82 lbs per minute until a total of 6250 lbs of the slurry had been charged. Charging of the 480 TBN slurry was followed by a 50 gallon charge of 5W oil to the reactor through the same line used to charge the slurry. Simultaneously with charging of the 480 TBN $Ca(OH)_2$/5W oil slurry, charged separately were 1020 lbs of ethylene glycol at a rate of 13 lbs per minute and separately carbon dioxide gas at a rate of 7000 SCFH. Following completion of the 480 TBN slurry and glycol charges, the CO_2 charge was allowed to continue until completion of the carbonation. Carbonation was deemed completed 5 minutes after the reactor off-gas exceeded 5000 SCFH. The product, vacuum stripped with nitrogen at 480 °F and filtered through Celite 535, had a final inspection as follows: Calcium (wt.%) 9.4; Sulfur (wt.%) 2.9; Glycol (wt.%) 0.6; Carbonate C (wt.%) 1.8; TBN (mg KOH/g) 272; PM Flash (°F) 360; Viscosity (cSt 100 °C) 106; BS&W (Vol. %) < 0.05.

Table I below sets forth a comparison of the reaction cycle times for the batch preparation of Example I and the present invention's batch preparation described in Example III.

TABLE I

Comparison of Reaction Cycle Time of Example I and Example III			
	Process Step	Ex. I	Ex. III
		(minutes)	
1.	Charge 5W oil, glycol and 180 TBN $Ca(OH)_2$ in Dodecylphenol Slurry	65	65
2.	Charge sulfur	15	60
3.	Heat reaction vessel to 330 °F for sulfurization reaction.	120-180	0
4.	Hold for reaction.	60	30
5.	Charge 480 TBN slurry of $Ca(OH)_2$ in 5W oil and glycol.	40	80
6.	Strip with N_2.	20	0
7.	Carbonate to off-gas breakthrough	60	40
8.	Repeat steps 5 to 7.	120	0
Reaction Cycle Time (min.)		500-560	275

Note that while both preparations processed the same amount of reactants resulting in essentially equivalent quantity and quality of product, the improvements of the present invention as carried out in Example III reduced the reaction cycle time by 225 to 285 minutes. This significant reduction is made possible by the novel and non-obvious manner in which the sulfurization and carbonation steps are carried out in the batch process of the present invention. In particular, the two stage carbonation required in the batch process of Example I is obviated in the present invention by conducting carbonation at the same time that the 480 TBN $Ca(OH)_2$/5W oil slurry and glycol are being charged to the reactor. This feature of the invention circumvents the problem of high viscosity in the batch reaction mixture, which problem necessitates a two stage carbonation as used in Example I, while avoiding the problem of over- or undercarbonation associated with a continuous process such as that described in Example II, which problem results in water tolerance difficulties in the phenate product.

A comparison was made of the water tolerance of the overbased phenate prepared in Example II (continuous process) with the water tolerance of the overbased phenate prepared by the present invention in Example III. Conventional treat levels of the two phenates were incorporated into a standard commercial lubricant formulation containing a major proportion of lube oil and a minor effective amount of ashless dispersant, low base calcium sulfonate, high base magnesium sulfonate, an oxidation inhibitor and zinc dialkyldithiophosphate. The water tolerance of the standard formulation containing the Example II overbased phenate was compared to the standard formulation containing the Example III overbased phenate by measuring haze and sediment in samples of the formulation after six weeks of storage at either 70 °F or 130 °F and at three different levels of water (0.10, 0.15, and 0.20 wt.%) in the formulation. Thus, for each overbased phenate six separate samples of the standard formulation were tested. The results of the water

tolerance tests are summarized in Table II, below.

TABLE II

Water Tolerance Test of Example II and Example III Phenates

	70°F Storage				130°F Storage			
	Water, wt.%			Rating**	Water, wt.%			Rating
	0.10	0.15	0.20		0.10	0.15	0.20	
Ex. II	A/tr*	A/tr	M/15	Good	A/tr	M/15	M/20	Bdln
Ex. III	A/tr	A/tr	A/tr	Ideal	A/tr	A/tr	M/20	Good

* Haze/sediment; Haze ratings begin with "A" for best clarity and any rating of "D" or higher is considered a failure. Sediment is measured in volume % and "tr" means trace of sediment. Sediment > 1% at any time during six week storage is failure.

** The ratings are assigned as follows:

Rating	Criteria
Ideal	No haze or sediment at any water level.
Good	Fails haze or sediment at 0.20% water.
Borderline	Fails haze or sediment at 0.15% water
Poor	Fails haze or sediment at 0.10% water.

The data set forth in Table II above demonstrate that the process of the present invention (Example III) results in an overbased phenate having significantly improved water tolerance than the phenate produced in the continuous process of Example II.

In view of the data set forth in Tables I and II above, the process of the present invention can significantly increase the throughput of a batch process while at the same time accomplishing the excellent water tolerance properties normally associated with a batch preparation.

Claims

1. A process for preparing an overbased sulfurized alkaline earth metal alkylphenate having excellent water tolerance properties in lubricant formulations, which process comprises the steps of:

a) charging into a reaction vessel a preheated mixture consisting essentially of alkaline earth metal base and alkylphenol in a mole ratio of 0.1:1 to 1.0:1 such that said mixture enters the reaction vessel at a temperature in the range of 280 to 380 °F (137.8 to 193.3 °C); while simultaneously, but separately, charging into said reaction vessel 0.1 to 1.0 mole of a promoter solvent per mole of alkylphenol; followed by

b) charging into said reaction vessel 1.0 to 2.0 moles of molten sulfur per mole of alkylphenol over a period in the range of 20 to 180 minutes at a rate that controls the reaction exotherm and off-gas evolution, while maintaining the reaction temperature within the range of 280 to 380 °F (137.8 to 193.3 °C);

c) upon completion of the sulfur charge, allowing the contents of the reaction vessel to interact at a reaction temperature within the range of 280 to 380 °F (137.8 to 193.3 °C) for a period of time sufficient to form sulfurized alkaline earth metal alkylphenate;

d) converting the sulfurized alkaline earth metal alkylphenate to overbased phenate by charging simultaneously into said reaction vessel while maintaining the reaction temperature within the range of 280 to 380 °F (137.8 to 193.3 °C) (i) 0.5 to 2 moles of alkaline earth metal base per mole of alkylphenol, (ii) 0.5 to 2.0 moles of promoter solvent per mole of alkylphenol; and (iii) 0.40 to 0.95 moles of carbon dioxide gas per mole of alkaline earth metal base, at a controlled charge rate not substantially greater or less than the rate at which the reactants present in the vessel undergo reaction to form the overbased phenate;

e) upon completion of said charging of alkaline earth metal base and promoter solvent to the reaction vessel, allowing said carbon dioxide charge to continue until completion of the carbonation reaction as evidenced by a sharp increase in the reactor off gas when the charged carbon dioxide is no longer being absorbed into the reaction medium;

f) stripping off unreacted alkylphenol and promoter solvent under vacuum with an inert gas purge at a temperature in the range of 400 to 480 °F (204.4 to 248.9 °C); and

g) filtering the resultant reaction product mixture and recovering the filtered product;

said process being still further characterized in that it is conducted with a reaction cycle time of no more than 6 hours; and in that said filtered product has water tolerance properties normally associated with a batch preparation of said product in which the process has a reaction cycle time of at least 8 hours.

2. The process of Claim 1 wherein the alkaline earth metal base is calcium hydroxide, the alkylphenol is dodecylphenol and the promoter solvent is ethylene glycol.

3. The process of Claim 2 wherein the molar ratio of calcium hydroxide to dodecylphenol in step (a) is 0.4 to 0.6:1; the molar ratio of ethylene glycol to dodecylphenol in step (a) is 0.4 to 0.6:1; the molar ratio of sulfur to dodecylphenol in step (b) is 1.3 to 1.6:1; the mole ratio of calcium hydroxide to dodecylphenol in step (d) is 1.0 to 1.5:1; the mole ratio of ethylene glycol to dodecylphenol in step (d) is 1.0 to 1.5:1; and the mole ratio of CO_2 charged in steps (d) and (e) to dodecylphenol is 1.0 to 1.5:1.

4. The process of Claim 1 wherein the reaction temper-atures in steps a), b), c) and d) are maintained within the range of 300 to 360 °F (148.9 to 182.2 °C).

5. The process of Claim 1 wherein the ratio of CO_2 to alkaline earth metal base charged in step d) is 0.75 to 0.85:1.

6. The process of Claim 1 wherein the alkaline earth metal base is an oxide or hydroxide of calcium or magnesium.

7. The process of Claim 1 wherein the reaction of step c) is conducted in the presence of a low base alkaline earth metal sulfonate.

8. The process of Claim 7 wherein said sulfonate is a calcium alkylbenzene sulfonate having an alkyl substituent in the range of C_{15} to C_{80}, and wherein the alkaline earth metal base is a calcium base.

9. The process of Claim 1 wherein the reactions of steps c) and d) are conducted in the presence of a lubricating oil reaction diluent.

10. The process of Claim 1 wherein the alkaline earth metal base is an alkaline earth metal oxide or hydroxide, wherein the promoter solvent is ethylene glycol, wherein the reaction temperatures in steps a), b), c) and d) are maintained within the range of 300 to 360 °F (148.9 to 182.2 °C), wherein the reaction of step c) is conducted in the presence of a low base alkaline earth metal sulfonate, wherein the reactions of steps c) and d) are conducted in the presence of a mineral lubricating oil reaction diluent, and wherein the ratio of CO_2 to said oxide or hydroxide of calcium charged in step d) is 0.75 to 0.85:1.

11. The process of Claim 10 wherein the alkaline earth metal base is a calcium base and wherein the alkaline earth metal sulfonate is a calcium alkylbenzene sulfonate having an alkyl substituent in the range of C_{15} to C_{80}.

12. The process of Claim 11 wherein said calcium base is calcium hydroxide and wherein said alkyl substituent is derived from a polymer of a C_2 to C_4 monomer.

13. The process of Claim 11 wherein the molar ratio of calcium hydroxide to the alkylphenol in step a) is 0.4 to 0.6:1; the molar ratio of ethylene glycol to the alkylphenol in step a) is 0.4 to 0.6:1; the molar ratio of sulfur to the alkylphenol in step b) is 1.3 to 1.6:1; the mole ratio of calcium hydroxide to the alkylphenol in step d) is 1.0 to 1.5:1; the mole ratio of ethylene glycol to the alkylphenol in step d) is 1.0 to 1.5:1; and the mole ratio of CO_2 charged in steps d) and e) is 1.0 to 1.5:1.

14. The process of Claim 11 or 13 wherein the alkylphenol is dodecylphenol.