# United States Patent [19]

**Hellmuth et al.**

[11] **3,764,536**

[45] **Oct. 9, 1973**


[54] **OVERBASED CALCIUM SALTS OF ALKENYLSUCCINIMIDE**


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[22] Filed: **Oct. 14, 1971**

[21] Appl. No.: **189,370**

[52] **U.S. Cl.**..... **252/49.7**, 252/51.5 A, 252/389, 252/18

[51] **Int. Cl.**..... **C10m 1/20**

[58] **Field of Search**..... 252/33.6, 34, 34.7, 252/49.7, 389, 51.5 A; 260/326.5 FU



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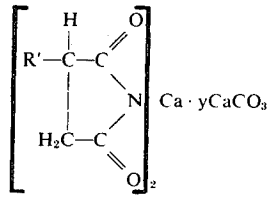


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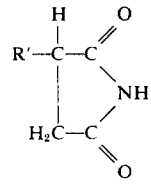


[57] **ABSTRACT**

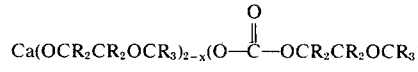
An improved dispersant and rust inhibiting additive for automotive lubricating oils comprising overbased calcium salt of alkenylsuccinimide characterized by the formula:



where R′ is alkenyl of from 30 to 300 carbons and *y* is an integer of from about 0.1 to 18, said overbased calcium salt prepared by contacting alkenylsuccinimide of the formula:



where R′ is as heretofore defined with a $CO_2$ blown calcium 2-alkoxyalkoxide complex characterized by the formula:



where R is H, $CH_3$ and/or $C_2H_5$ and *x* is from 0.5 to 1.5 at a temperature of between about 50° and 180°C. in the presence of water and preferably in the presence of an inert liquid diluent.

**9 Claims, No Drawings**

# OVERBASED CALCIUM SALTS OF ALKENYLSUCCINIMIDE

## BACKGROUND OF INVENTION

Mineral lubricating oil employed as crankcase lubricants in internal combustion engines tend to oxidize at the high temperatures to which they are subjected in this type of service with the resultant formation of gums, sludges which clog the oil feed lines and form varnish-like deposits on the surfaces of rings, pistons, cylinders and other engine parts. Further, with emission control devices being installed on the presently manufactured automotive vehicles, much of the corrosive bodies of the engine exhuast system are not introduced into the crankcase oil. The gums and sludges lead to piston sticking and varnish on the cylinder walls. This coupled with the attack of the corrosive bodies on the engine metal surfaces cause substantial deterioration of the engine operation.

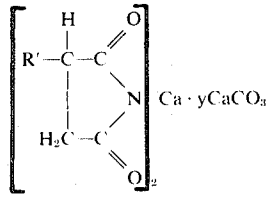
In order to counteract these negative factors, additives are added to crankcase oils in small amounts such as dispersants to counteract the formation of gums and sludges and anticorrosives to inhibit the corrosive action of the exhaust gases introduced into the crankcase system. One of the suitable known dispersants are the normal metal salt derivatives of the alkenylsuccinimide where the alkenyl portion ranges from 15 to 30 carbons as represented in U. S. Pat. No. 2,628,942.

Hereinbefore and hereinafter the term "normal" when referring to the salt of the alkenylsuccinimide denotes the ratio of the number of equivalents of metal moiety to the number of equivalents of alkenylsuccinimide moiety is about 1 and the term "overbased" when utilized in connection with the alkenylsuccinimide salts denotes the ratio of the number of equivalents of metal moiety to the number of equivalents of alkenylsuccinimide moiety is greater than about 1.

Although the prior normal metal alkenylsuccinimide as represented in U. S. Pat. No. 2,628,942 are satisfactory as crank-case dispersants, there is a need due to the burden placed by auto emission control devices on crankcase oils to also incorporate anticorrosive properties in such type additives.

## SUMMARY OF INVENTION

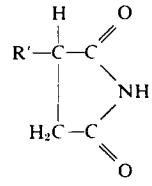
We have discovered and this constitutes our invention a novel additive for lubricating oils having superior dispersancy and corrosion inhibiting properties for use in crankcase oils for automotive, diesel and airplane engines. Further, we have discovered a method for manufacturing said additive and lubricant compositions resulting therefrom. Specifically, the novel additive of the invention having detergent-dispersant and rust inhibiting properties is the overbased calcium salt of alkenylsuccinimide characterized by the formula:



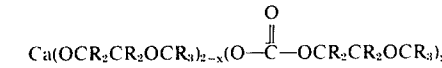



where R is alkenyl of from 30 to 300 carbons and $y$ is an integer of from about 0.1 to 18.

The overbased calcium salt additives are prepared by contacting alkenylsuccinimide characterized by the formula:




with $CO_2$ blown calcium 2-alkoxyalkoxide characterized by the formula:

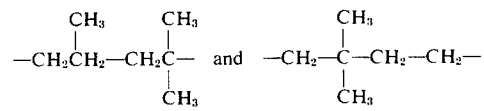



where R is H, $CH_3$ and/or $C_2H_5$, x is an integer of from about 0.5 to 1.5 and water initially utilizing an imide to $CO_2$ blown calcium reagent to water mole ratio of between about 1:0.5:0.1 and 1:9.5:12 at a temperature between about 50 and 180°C., normally for a period of between about 1 and 3 hours. Under preferred conditions, the reaction is conducted under conditions of agitation and in the presence of an inert liquid diluent. The inert diluent when employed advantageously constitutes between about 10 and 50 vol. % of the reaction mixture.

At the end of the reaction period, the crude product is preferably stripped with inert gas blowing such as nitrogen blowing, preferably under reduced pressure, to remove volatile materials therefrom. The resultant overbased products, normally in liquid form, are desirably filtered via standard means to remove any solid impurities therefrom.

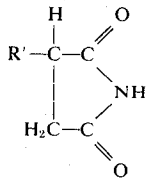
One of the essential features in the manufacturing process is the employment of the $CO_2$ blown calcium reagent as defined. Substitution of normally considered overbasing equivalents such as calcium oxide, calcium hydroxide or calcium oxide and calcium hydroxide solutions in lower alkanol will produce the normal calcium salts of alkenyl-succinimide as disclosed in U. S. Pat. No. 2,628,942 but not the desired overbased calcium salts.

The alkenylsuccinimide reactants are prepared by standard means such as reacting the maleic anhydride with a polyalkene polymer of from 30 to 300 carbons, e.g., containing three to five carbon atoms repeating groups, such as




at an elevated temperature, e.g., 200° to 300°C. and then subsequently passing ammonia through the resultant solution at a temperature between about 100° and 250°C. to form the alkenylsuccinimide as heretofore defined.

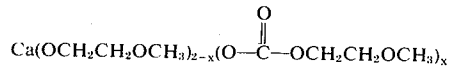
Specific examples of the succinimide reactant characterized by the formula:



are where R′ is polyisobutene of an average molecular weight of about 500, R′ is polyisobutylene of an average molecular weight of about 800, R′ is polyisobutene of an average molecular weight of about 1200, R′ is polypropylene of an average molecular weight of about 1500, R′ is polypentylene of an average molecular weight of about 2000 and R′ is polybutene of an average molecular weight of about 3000.

The $CO_2$ blown calcium-2-alkoxyalkoxide reagent is prepared by the reaction of calcium carbide and 2-alkoxy-alkanol utilizing a temperature of between about 150° and 250°F. and a mole ratio of alcohol for calcium carbide of between about 3:1 and 100:1. The resultant mixture is then blown with carbon dioxide at a temperature between about 50° and 150°C. utilizing a calcium to carbon dioxide mole ratio of between about 0.5:1 and 1.5:1 to form the $CO_2$ blown reagent as precedingly defined.

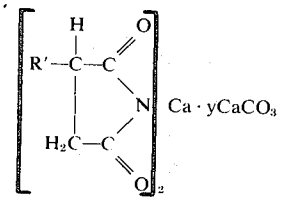
Examples of the calcium reagent characterized by the formula:



are where $x$ is 0.5, $x$ is 1, $x$ is 1.2 and $x$ is 1.5 where R is respectively H, $CH_3$, $C_2H_5$.

Examples of the solvent suitable in the manufacture of the overbased calcium additive are benzene, toluene and other alkyl substituted liquid aromatic hydrocarbons; hydrocarbon lubricating oil of an SUS viscosity of between about 50 and 500 at 100°F.; alkanes such as heptane, isooctane, etc. as well as saturated cyclic and alicyclic hydrocarbon solvents such as cyclohexane, methylcyclohexane, etc. When lubricating oils are employed, a lube oil concentrate of overbased calcium succinimide is formed as the final product. Volatile substances such as benzene, toluene and cyclohexane are removed during stripping.

Examples of the overbased calcium salt product of the invention characterized by the formula:



are where R′ is polyisobutene of an average molecular weight about 500 and $y$ is 0.5; R′ is polyisobutene of an average molecular weight of about 800 and $y$ is 1; R′ is polyisobutene of an average molecular weight of about 1200 and $y$ is 2; R′ is polypropylene of a molecular weight of about 2000 and $y$ is 2.5; R′ is polybutene of an average molecular weight of about 3000 and $y$ is 3.5.



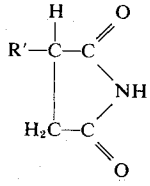
In the formulation of the lubricant composition of the invention, suitable base oils include a wide variety of hydrocarbon lubricating oils such as naphthetic base, paraffinic base and mixed base mineral oils or other hydrocarbon lubricants, e.g., lubricating oil derived from coal products and synthetic hydrocarbon oils, e.g., alkylene polymers such as polypropylene, polyisobutylene of a molecular weight of between about 250 and 2500. Advantageously, the lubricating oils having an SUS viscosity at 100°F. between about 50 and 2000 are employed. The overbased calcium additives are incorporated in the base oils in an amount of between about 0.5 and 20 wt. %, preferably between about 0.5 and 5.0 wt. %. In the finished lubricating oil compositions other additives may be included. These other additives may be any of the standard suitable pour depressors, supplementary sludge dispersants, antioxidants, silver corrosion inhibitors, viscosity index improvers and friction modifiers. Exactly what other additives are included in the finished oil compositions and particular amounts thereof will, of course, depend on the particular use and conditions desired for the finished oil products.

The following examples further illustrate the product, method of producing and lubricant compositions thereof but are not to be construed as limitations thereof.

## EXAMPLE I

This example illustrates the preparation of the alkenylsuccinimide reactant.

Into 5280 grams (2.0 mole) of polyisobutene (1200 m.w.) succinic anhydride dissolved in polyisobutene (1200 m.w.), heated to 100°C. there was introduced at a rate of 500 mls./min. ammonia for 1 hour, then at 140°C. for 0.5 hour and at 180°C. for 0.5 hour. The resultant ammonia treated reaction mixture was then flushed with nitrogen for 15 minutes and filtered through diatomaceous earth. Approximately 5000 grams of product were recovered and analysis found it to contain 0.56 wt. % nitrogen. It was identified as polyisobutene (1200 m.w.) succinimide characterized by the formula:



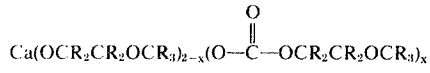
where R′ is polyisobutene of an average molecular weight of about 1200.

## EXAMPLE II

This example illustrates the preparation of the $CO_2$ blown calcium-2-alkoxyalkoxide reagent.

To 150 lbs. of 2-methoxyethanol there was introduced 25 lbs. of finely divided calcium carbide and the reaction mixture was stirred at 251°–253°F. for 1 hour. To the resultant product weighing 164 lbs. and identified as calcium 2-methoxyethoxide there was introduced $CO_2$ at a rate of 11 lbs. per hour for 1.5 hours at 258°F. At the end of the reaction period the resultant product was filtered through diatomaceous earth and

was identified as $CO_2$ blown calcium2-methoxyethoxide characterized by the formula:

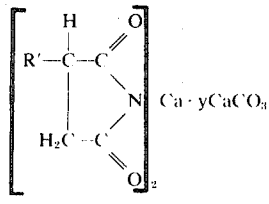


where $x$ is 1 and analyzed 8.0 wt. % Ca.

## EXAMPLE III

This example illustrates the preparation of an overbased calcium alkenylsuccinimide species.

To 259 grams (0.10 mole) of polyisobutene (1200 m.w.) succinimide solution of the type prepared in Example I dissolved in 100 mls. of toluene there was added 100 grams of $CO_2$ blown calcium 2-methoxyethoxide of the type prepared in Example II and 3.3 mls. (0.15 mole + 25 percent mole excess) water. The resultant mixture was stirred 1 hour at 100°C., stripped with nitrogen blowing to a temperature of 180°C., then stripped using a water aspirator (20 mm Hg) to 180°C. and filtered through diatomaceous earth. The recovered liquid product weighed 262 grams and was characterized by the formula:



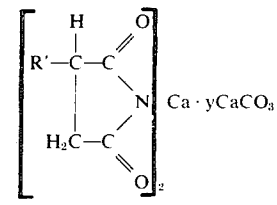
where R′ is polyisobutene (1200 m.w.) and y is 3.0. Analysis of the product found a nitrogen content of 0.49 wt. % (0.51 calc.) and a calcium content of 3.0 wt. % (2.91 calc.).

## EXAMPLE IV

This example further illustrates the preparation of the overbased calcium alkenylsuccinimide and the lube oil concentrate.

To 1000 grams of naphthenic oil having an SUS viscosity of 100 at 100°F. there was added 259 grams (0.102 mole) of polyisobutene (1200 m.w.) succinimide solution as prepared in Example I. The resultant mixture was heated to 90°C. and there was added 50 mls. of $CO_2$ blown calcium 2-methoxyethoxide as prepared in Example II. The resultant mixture was heated to 90°C. for a period of 15 minutes whereupon an additional 50 mls. of calcium reagent and 5 mls. of water were added. The temperature was again held at 90°C. for 15 minutes. The calcium reagent and water additions and stirring period were repeated four more times and the resultant mixture was stripped with nitrogen blowing to 180°C., filtered through diatomaceous earth and 60 grams of solid product were removed on the filter. A total of 250 grams of calcium reagent and 18 grams of water are employed. The resultant liquid filtrate was identified as a lube oil solution containing about 15 wt. % of an overbased calcium polybutene (1200 m.w.) succinimide characterized by the formula:



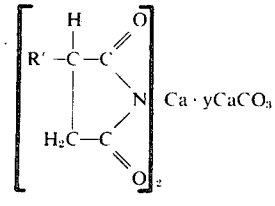


where R′ is polyisobutene of an average molecular weight of about 1200, $y$ is 4. The product was analyzed and found to contain 0.10 wt. % nitrogen (calc. 0.094) and 0.7 wt. % calcium (calc. 0.9).

## EXAMPLE V

This example further illustrates the preparation of the calcium overbased alkenylsuccinimide.

To 368 grams (0.1 mole) of polyisobutene (1200 m.w.) succinimide solution heated to 80°C. there was added 24.4 grams of $CO_2$ blown calcium 2-methoxyethoxide of the type prepared in Example II over a 5 minute period and the resultant mixture was stirred 5 minutes, stripped with nitrogen to 150°C., cooled to 90°C. Then 24.5 grams of calcium reagent of the type perpared in Example II simultaneously with 5 mls. of water and 25 mls. of 2-methoxyethanol were added over 5 minutes and the aforedescribed stirring, stripping and cooling sequence were repeated until a total of 146 grams of calcium reagent, 25 mls. of water and 125 mls. of 2-methoxy-ethanol were added. The resultant mixture was then stripped to 180°C. with $CO_2$ blowing (1000 mls./min.) and filtered through diatomaceous earth. The resultant product filtrate was recovered in an amount of 258 grams and was identified as characterized by the formula:



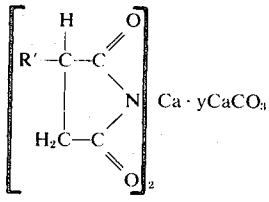
where R is polyisobutene in an average molecular weight of about 1200 and $y$ is 6. Further analysis of the product found it to contain 2.8 wt. % calcium (3.95 calc.) and 0.29 wt. % nitrogen (0.35 calc.).

## EXAMPLE VI

This example illustrates the preparation of overbased calcium polyisobutene succinimide.

Three hundred sixty eight grams (0.10 mole) of polyisobutene (1200 m.w.) succinimide were heated to 90°C. and there were added 24.4 grams of $CO_2$ blown calcium 2-methoxyethoxide of the type produced in Example II. The resultant mixture was stirred 10 minutes, stripped to 150°C. with carbon dioxide blowing (500 mls./min.) and the temperature reduced to 90°C. There was then added additional 24.4 mls. of calcium reagent of Example II and 5 mls. water and 25 mls. of 2-methoxyethanol simultaneously over a 5 minute period. The resultant mixture was stripped and cooled as before and repeated until all the calcium reagent and water solution was employed and the resultant mixture was stripped to 180°C. with $CO_2$ blowing and the resultant mixture was filtered through diatomaceous earth

with the recovery of 288 grams of product. A total of 97.6 grams of calcium reagent (0.4 equivalents) were utilized. The product was analyzed and determined to be overbased calcium polyisobutene (1200 m.w.) succinimide characterized by the formula:




wherein R' is polyisobutene of an average molecular weight of about 1200 and y is 2.5. Analysis of the mixture found 1.4 wt. % Ca, 0.28 wt. % N.

## EXAMPLE VII

This comparative example illustrates the importance of employing the method of the invention to prepare the overbased calcium alkenylsuccinimide.

To 269 grams of polyisobutene (1200 m.w.) succinimide (0.10 mole) solution there was charged 14 grams calcium oxide (0.25 mole), 100 grams ethylene glycol (1.6 mole), 100 mls. toluene and 4.5 mls. water (0.25 mole + 25 mole % excess). The resultant mixture was refluxed at about 115°C. for 3 hours with $CO_2$ blowing (500 mls./min.) then stripped to 100°C. utilizing a water aspirator (20 mm Hg). Eighty five mls. of toluene and 864 grams of polar material were stripped out. The product was unfilterable and of a grease-like quality. No useful lubricating oil additive as obtained by this process.

The foregoing procedure was repeated utilizing 233 grams of polyisobutene (1200 m.w.) succinimide, 14 grams calcium oxide, 100 mls. ethylene glycol, 100 mls. toluene, 4.5 mls. water and 149 grams of naphthenic mineral oil having an SUS viscosity at 100°F. of 100. The resultant mixture was refluxed for 3 hours at about 120°C. while simultaneously passing 700 mls./min. $CO_2$ therethrough. The resultant mixture was stripped to 180°C. utilizing a water aspirator (20 mm Hg). The resultant product would not filter and analysis indicated that no overbased product was formed.

## EXAMPLE VIII

This example illustrates the lubricant compositions of the invention contemplated herein and also illustrates the function of the overbased calcium alkenylsuccinimide as an effective dispersant in lubricating oils.

The test procedure employed comprises introducing into a bottle the test lubricating oil compositions, titanium oxide (6 wt. %) in oil and engine blowby. The bottle was agitated at an elevated temperature for a period of time and a portion of the bottle contents was centrifuged. Upon centrifuging, three phases are formed, i.e., a top clear oil phase, a middle dirty oil phase in which sludge remains dispersed and a bottom sediment phase. The clear oil and sediment depth are measured in millimeters and recorded as the first cycle. For the second and subsequent cycles to the sample remaining in the bottle from the first cycle portions of the following materials were added in the order listed: titanium oxide (6 wt. %) in oil and engine blowby and the procedure of the first cycle is repeated. The cycles are continued until the centrifugal oil is clear and completely free of sediment. The greater the depth of sediment and clear oil in the centrifuged tube the less the dispersant capacity of the test oil composition.

The base oil composition employed on the foregoing test to which the overbased calcium alkenylsuccinimide is added is of the following composition:

TABLE I

| Description | Wt. % |
|---|---|
| Paraffinic Oil (~140 SUS at 100°F.) | 89 |
| $CO_2$ blown 1:1 overbased barium alkylphenolate | 6 |
| Zinc dialkyldithiophosphate | |
| $CO_2$ blown 1:1 overbased barium sulfonate | |
| 750 ppm Silicone polymer antifoamant | |
| Copolymers of butyl to stearyl methacrylate (3500 SUS at 210°F.) | 5 |

TABLE II

| Run No. | Base Oil Comp. | Overbased Ca Additive Wt. %* | Bench Sludge Test | Cycle | 1 | 2 | 3 | 4 |
|---|---|---|---|---|---|---|---|---|
| A | 100 | 0 | | Clear | 41 | 38 | — | — |
| | | | | Sediment | 9 | 2 | — | — |
| B | 96.6 | 3.4 | | Clear | 2 | 3 | 6 | 37 |
| | | | | Sediment | 4 | 9 | 8 | 11 |

*Product Ex. III

## EXAMPLE IX

This example illustrates the rust inhibiting properties of lubricant compositions containing the overbased calcium alkenylsuccinimide and also illustrates lubricant compositions containing said succinimide.

The rust test employed is a low temperature engine procedure which comprises lubricating a 1964 289 CID V-8 engine. The engine is run under the following test conditions.

TABLE III

| Description | Value |
|---|---|
| Duration, hrs. | 45 |
| Speed, rpm | 1500 |
| Load, BHP | 28 |
| Fuel pressure, psi | 4.5 |
| Fuel/air ratio | 0.085 |
| Crankcase Ventilation, °F. | |
| Jacket Out | 90 |
| Oil Gallery | 110 |
| Rocker Arm Covers | 60 |
| Intake Air | 110 |

At the end of the test period of the various engine runs the external and internal area of the valve lifters and push rods were inspected. A rating of 10 represented no rusting and a rating of zero indicated heavy rusting of the entire surfaces. Three compositions were subjected to this test. These formulations (Oils C, D and E) all consisted of the same base composition, namely, a paraffinic lubricating oil of ~130 SUS viscosity at 100°F. containing a zinc dialkyl dithiophosphate, supplementary ashless dispersant and methacrylate VI improver. Additionally, in Oil C there was also present an overbased succinimide of the type described in Example III but R' was at 400 m.w. polybutene. In Oil D a comparative rust preventive compound, calcium overbased $P_2S_5$-polybutene (400 m.w.), was present.

The calcium level in both Oils C and D was 0.175 wt. %. Oil E was said base composition per se.

The test results in this rust test are as follows:

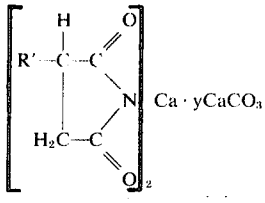
TABLE IV

| Oil | Additive Wt. % Ca | Test Hours | Internal | External |
|---|---|---|---|---|
| C | 0.175 | 45 | 3.9 | 8.7 |
| D | 0.175 | 45 | 3.6 | 8.2 |
| E | 0 | 21 | 4.5 | 7.8 |
| | | 20 | 3.9 | 5.7 |
| | | 20 | 4.7 | 5.4 |

The above demonstrates the utility of overbased alkenylsuccinimide products to prevent rusting in automotive engines.

We claim:

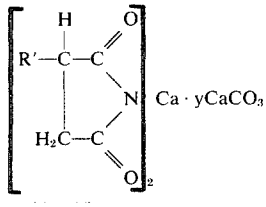
**1.** An overbased calcium alkenylsuccinimide characterized by the formula:




where R′ is alkenyl of from 30 to 300 carbons and *y* is an integer of from 0.1 to 18.

**2.** A compound in accordance with claim **1** wherein R′ is polyisobutene of an average molecular weight of about 1200.

**3.** A lubricating oil composition comprising a major amount of a refined mineral lubricating oil and a small amount sufficient to improve detergency and rust inhibition thereof of an overbased calcium alkenylsuccinimide characterized by the formula:

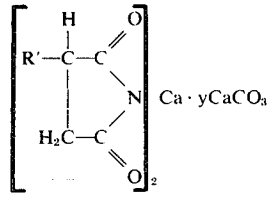



where R′ is alkenyl of from 30 to 300 carbons and y is an integer of from 0.1 to 18.

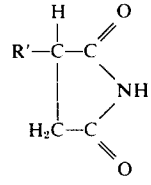
**4.** A lubricant composition according to claim **3** containing between about 0.5 and 10 wt. % of said additive.

**5.** A lubricant composition according to claim **3** wherein R′ is polyisobutene of an average molecular weight of about 1200.

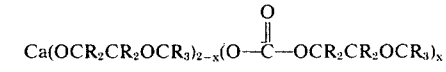
**6.** A method of producing overbased calcium alkenyl-succinimide characterized by the formula:




where R′ is alkenyl of from 30 to 300 carbons and y is an integer of from about 0.1 to 18 comprising contacting an alkenylsuccinimide of the formula:




where R′ is as heretofore defined with a $CO_2$ blown calcium methoxyethoxide characterized by the formula:




where R is H, $CH_3$, and/or $C_2H_5$, where *x* is between about 0.5 and 1.5 in the presence of water at a temperature between about 50° and 180°C. utilizing a mole ratio of said alkenyl-succinimide to calcium reagent to said water to between about 1:0.5:0.1 and 1:9.5:12.

**7.** A method in accordance with claim **6** where R is H.

**8.** A method in accordance with claim **7** where said contacting is conducted in the presence of inert liquid diluent in an amount of between about 10 and 50 vol. % of the reaction mixture.

**9.** A method in accordance with claim **8** wherein said solvent is toluene, hydrocarbon mineral lubricating oil, or 2-methoxyethanol and said R′ is polyisobutene of an average molecular weight of about 1200.

* * * * *

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(5/69)

# UNITED STATES PATENT OFFICE
# CERTIFICATE OF CORRECTION

**Patent No.** 3,764,536 **Dated** October 9, 1973

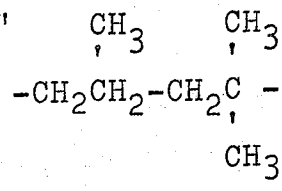
**Inventor(s)** WALTER W. HELLMUTH and ELMER E. SCHALLENBERG

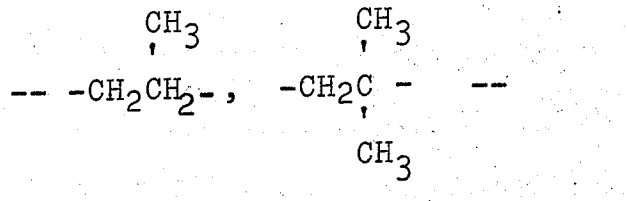
**It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:**

Col. 1, line 14, "exhuast" should read --exhaust--.

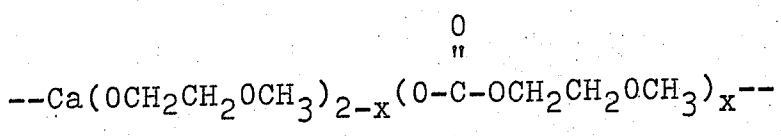
Col. 1, line 41, "crank-case" should read --crankcase--.

Col. 2, line 55, " should read





Col. 5, line 6, "$Ca(OCR_2CR_2OCR_3)_{2-x}(O-\overset{O}{\overset{\|}{C}}-OCR_2CR_2OCR_3)_x$" should read



# UNITED STATES PATENT OFFICE
# CERTIFICATE OF CORRECTION

Patent No. 3,764,530 Dated October 9, 1973

Inventor(s) Walter W. Hellmuth and Elmer E. Schallenberg

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Col. 8, Table II, lines 24-25 "Over-" in the first column (line 24) of Table II should be located directly above "based" (line 25), 3rd column of Table II.

Signed and sealed this 30th day of April 1974.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents

FORM PO-1050 (10-69)

USCOMM-DC 60376-P69
* U.S. GOVERNMENT PRINTING OFFICE : 1969 O—366-334.