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HYDROCARBON OIL COMPOSITIONS CONTAINING TELOMERIC POLYALKYL OXOESTERS AS ANTI-FOAMING AGENTS

Joseph E. Fields and Tracy M. Patrick, Jr., Dayton, Ohio, assignors to Monsanto Chemical Company, St. Louis, Mo., a corporation of Delaware

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12 Claims. (Cl. 252—56)

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This invention relates to antifoaming hydrocarbon oils and deals more particularly with hydrocarbon oils containing small amounts of liquid telomeric polyalkyl oxoesters.

The problem of foam inhibition is one of major importance to all industries employing hydrocarbon oils under foam-inducing conditions. While most oils will foam to some extent due to vigorous agitation and aeration in a running engine, foaming becomes a problem only when loss of oil occurs by foam seepage or when so many air bubbles are present in the oil that proper lubrication of bearing surfaces is impeded. Foaming is often experienced with dry sump engines in which there is employed a scavenger pump for collecting oil from various engine parts and returning it to the lubricant reservoir. Here air may be collected along with the oil and deposited in the reservoir. The design and operation of aircraft engines is such that foaming occurs more readily in this type of engine than it does in automotive engines.

Foam and froth in hydrocarbon oils, however, is not due solely to engine design. Although location and design of the oil pump, oil sump and oil lines as well as modification of other engineering features may retard foam development, when certain oils are employed with high speed engines, mechanical control, alone, does not suffice. Here, the nature of the crank-case oil is often the prime factor in foaming difficulties. The heavier the grade of the oil or the higher the viscosity of the oil, the more difficult it is to avoid foaming. Heavy grade oils, such as those employed in high-speed diesel and spark ignition engines operating under severe conditions are particularly susceptible to foaming. The heavy oils hold bubbles very firmly so that when foam is formed, it is very persistent.

New developments in engine construction have constantly demanded lubricants having properties not possessed by crude hydrocarbon oils. Such properties are now generally conferred to lubricants by the use of additives. For example, in order to satisfy the lubrication requirements of hypoid gears, materials, which impart extreme-pressure resisting properties are now generally added to gear lubricants. In most cases, however, the improvement attained in an oil by the use of additives is made only at the expense of increasing its susceptibility to foam. Thus, while the demands of modern engine design for extreme pressure resisting lubricants, for anticorrosive lubricants, for lubricants of increased viscosity and low pour-point and good detersive properties have been met by the for-

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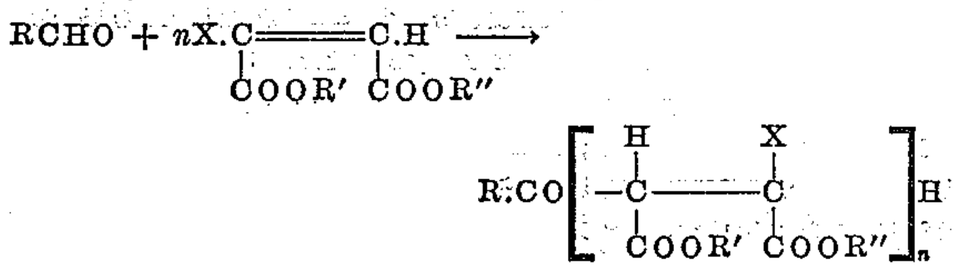
mulation and use of numerous chemicals which give these desirable properties to oils when admixed therewith, the use of such additives makes the treated oils particularly susceptible to foaming. While light grade oils, e. g., SAE 10 grade oils are almost non-foaming under the most severe conditions, when there are employed with these oils one or more additives such as viscosity index improvers, extreme pressure resisting improvers, pour-point depressors, etc., the resulting "improved" oils do not retain their non-foaming characteristics and are frequently even more susceptible to foaming than are the heavy grade oils.

Hence, with the development of new high-speed engines and the provision of the new additive-type lubricants, the problem of foaming has assumed major importance. Attempts to solve the problem by defoaming existing oils, e. g., by submitting oils to heat-treatment, absorption processes, filtering steps, etc., have proved of but little value. The most practical solution to this problem has been made by the use of antifoam additives.

A number of antifoam additives, i. e., antifoaming agents, foam depressing agents, foam depressants, antifrothers or foam suppressors, are known; but in prior art their use has been attended with numerous difficulties. Among disadvantages of such known additives are chemical reactvity with the lubricant or other oil additives, corrosive effect, susceptibility to decomposition upon heating, instability when exposed for long periods of time to ordinary atmospheric conditions, high cost, etc.

Now we have found that foaming of hydrocarbon oils is efficiently retarded and even completely inhibited when there is added to such oils a small quantity, say, from 0.001 per cent to 1.0 per cent by weight of a liquid mixture of telomers prepared by reaction of one mole of a saturated, aliphatic aldehyde of from 2 to 13 carbon atoms, with more than one mole of certain esters of α,β-unsaturated aliphatic, dicarboxylic acids. Telomers of this kind are described in the copending application of Tracy M. Patrick, Jr. and Earl W. Gluesenkamp, Serial No. 200,101, filed December 9, 1950. They are readily obtained by a free radical catalyzed addition reaction, substantially according to the scheme:



in which R is an alkyl radical of from 1 to 12 carbon atoms, X is selected from the class consisting of hydrogen and the methyl radical and R′ and R″ are selected from the class consisting of alkyl, cycloalkyl, aryl, alkaryl and aralkyl radicals of from 1 to 18 carbon atoms and *n* is an integer greater than one.

Saturated aldehydes which may be employed for the preparation of the present adducts are, for example, acetaldehyde, propionaldehyde, n-butyraldehyde, isobutyraldehyde, n-valeraldehyde, isovaleraldehyde, methylethylacetaldehyde, trimethylacetaldehyde, n-caproic aldehyde, isohexaldehyde, 2-ethylhexaldehyde, octaldehyde, capric aldehyde, undecaldehyde, lauric aldehyde, palmitic aldehyde, stearic aldehyde, etc. Esters which react with the above aldehydes to yield telomers which are useful for the present purpose are, for example, dimethyl, diethyl, diisopropyl, di-n-butyl, bis(2-ethylhexyl), dicyclohexyl, dibenzyl, di-p-tolyl, dihexadecyl, and didodecyl maleate; dimethyl, diisobutyl, dioctadecyl, diphenyl and dicyclopentyl fumarate, dipropyl, dioctlyl, bis(2-phenylethyl) and di-α-naphthyl citraconate, dimethyl, diundecyl, dixenyl and dibenzyl mesaconate, etc.

The liquid telomeric polyalkyl oxoesters are effective antifoaming agents when they are employed in very low proportions, i. e., in amounts of up to 1.0 per cent by weight, based on the weight of the total hydrocarbon oil composition. From .01 per cent to .10 per cent of the telomeric esters is preferred, depending upon the nature of the oil. Heavy oils and oils containing foam-inducing adjuvants require more of the present antifoaming adducts than do base oils of good viscosity characteristics.

Particularly valuable as antifoaming additives for hydrocarbon oils are liquid telomeric polyalkyl oxoesters in which one mole of a saturated, unsubstituted aliphatic aldehyde of from 2 to 12 carbon atoms has combined with from 2 to 30 moles of an ester selected from the class consisting of dialkyl and dicycloalkyl maleates, fumarates, mesaconates and citraconates in which each alkyl radical and each cycloalkyl radical has from 1 to 12 carbon atoms. The dialkyl and dicycloalkyl maleates in which each alkyl radical has from 1 to 8 carbon atoms are commercially available, inexpensive starting materials, and telomers prepared from such maleates are the preferred antifoaming agents at present.

The antifoaming effect of the aldehyde-ester telomers is not materially affected by the presence of other adjuvants in the oil. The liquid telomers are stable polyesters which can be hydrolyzed only with difficulty, and since they are present in the oils in only very small quantities, the use of even very acidic or very basic additions in the oil has substantially no effect on the telomers. Hydrocarbon oils containing the present antifoaming agents are stable when stored over long periods of time and also when subjected to heat and pressure conditions of engine and motor operation.

While the antifoaming effect of the liquid telomers is obtained when they are employed in concentrations of up to 1.0 per cent by weight, they may be incorporated into hydrocarbon oils in much higher proportions, e. g., in amounts of up to 10 per cent or even 50 per cent of the weight of the hydrocarbon oil to give concentrates. Oils containing such high proportions of the telomers may be manufactured and sold for use as lubricant additives. Addition of small amounts of such concentrates to hydrocarbon oils may be made so as to supply an oil containing suitable quantities of the telomers.

Hydrocarbon oils which are rendered substantially antifoaming by incorporation therein of quantities of up to 1.0 per cent of the present telomeric oxoesters are synthetic or petroleum stocks of varying viscosities such as lubricating oils for internal combustion engines and motors, diesel fuels and lubricants and pressure transfer media, e. g., industrial lubricants, process oils, hydraulic oils, turbine oils, cutting oils, fluid greases, gear oils, shock absorber oils, spindle oils, journal bearing oils, pneumatic tool lubricants, etc. They may be synthetic or natural hydrocarbons of any type, i. e., paraffinic, naphthenic or blended.

The invention is further illustrated, but not limited, by the following example.

Example

The antifoaming properties of lubricants may be determined according to the procedure generally described in Designation L-12-445 of the Coordinating Lubricants Research Committee of the Coordinating Research Council, New York. Briefly this procedure involves bubbling air or an inert gas such as nitrogen through the hydrocarbon oil to be tested, employing standard apparatus and standard conditions.

The oil was placed in a standard 100-ml. graduated cylinder in the top of which was inserted a two-hole rubber stopper. An air-inlet tube extended through this stopper, to the bottom of which was attached a gas diffuser or porous stone sphere. The length of the inlet tube was adjusted so that when the apparatus was assembled, the sphere just touched the bottom of the cylinder. The sphere was attached to the inlet tube by means of litharge or glycerine, or by a copper tube soldered to the diffuser-stone coupling. The oil bath used was capable of controlling temperature at 200°±1° F. (93.3°±0.6° C.), large enough to permit the cylinder to be immersed at least to the 90 ml. mark, and arranged to permit the visual observation of the graduations on the cylinder.

Dry nitrogen or air was supplied at the rate of 0.2 cubic foot per hour, employing a calibrated flowmeter. The sample was heated to 120° F. (48.9° C.), and then cooled, before testing, to 75°±5° F. (23.9°±2.8° C.) in a constant temperature room. 25 cc. of oil was used for each test.

With the air hose disconnected between the flowmeter and the delivery tube to the diffuser stone, the stone was allowed to soak in the oil for 5 minutes, at the end of which time the air flow (0.2 cu. ft. per hour) was started through the stone. Zero time was noted when the air or nitrogen bubbles started to rise from the stone. Readings of the top and bottom foam levels were taken at the end of a 5-minute period. The volume of foam was calculated from the two readings.

Employing the testing procedure described above, there were determined the antifoaming effects of various aldehydemaleate telomers when added to a Champlin 30 SAE base oil in concentrations of from 0.05% to .005% by weight of the oil. The telomers were prepared by heating mixtures of the aldehyde and maleate indicated below in the presence of benzoyl peroxide as catalyst, and removing from the resulting reaction mixture any unreacted material and 1:1 addition product by distilling the mixture up to

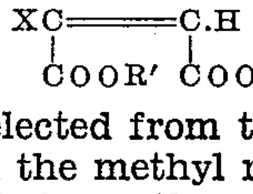
the head temperatures shown below, as described in the previously cited copending application.

Telomer No.	Reactants Used		B. P. of Telomer, above Head Temp. of—
	Aldehyde	Maleate	
1	Butyraldehyde	Dicyclohexyl	185° C./1 mm.
2	do	bis-2-(Ethylhexyl).	184° C./0.5 mm.
3	Heptaldehyde	do	210° C./0.7 mm.
4	2-Ethylhexaldehyde.	Diethyl	136° C./0.8 mm.

The following antifoaming values were obtained with these telomers:

Additive, Telomer No.	Foam (cc.) in 5 Min. Additive in p. p. m. of oil			
	None	500	200	50
None	75			
1		0	2–5	5–20
2		0	2–5	5–20
3		0	2–5	5–20
4		0	2–5	5–20

Nonfoaming hydrocarbon oil compositions are also obtained by incorporating into such oils in a quantity of up to 1.0 per cent, based on the weight of the composition, telomers of other saturated aliphatic aldehydes of from 2 to 13 carbon atoms and other dicarboxylates having the general formula

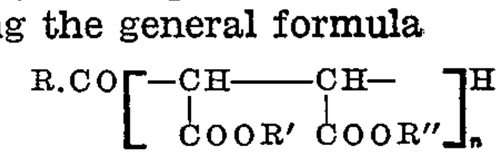


in which X is selected from the class consisting of hydrogen and the methyl radical and R′ and R″ are selected from the class consisting of alkyl, cycloalkyl, aryl, alkaryl and aralkyl radicals of from 1 to 18 carbon atoms. Thus instead of the telomers tested above, there may be advantageously employed, e. g., telomers of acetaldehyde and didodecyl fumarate, propionaldehyde and di-4-tolyl citraconate, n-valeraldehyde and dinaphthyl mesaconate, lauric aldehyde and dimethyl fumarate, etc. The present telomers impart antifoaming properties to hydrocarbon oils, generally, in the presence or absence of other customarily employed additives such as extreme-pressure resisting additives, detergent additives, etc.

This is a continuation-in-part of our application Serial No. 217,324, filed March 23, 1951, now abandoned.

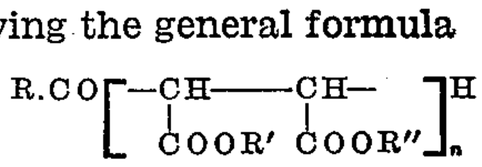
What we claim is:

1. A hydrocarbon oil composition containing up to 1.0 per cent by weight, based on the total composition, of a liquid telomeric polyalkyl oxoester having the general formula



in which R is an alkyl radical of from 1 to 12 carbon atoms, and R′ and R″ are selected from the class consisting of alkyl, cycloalkyl, aryl, alkaryl and aralkyl radicals of from 1 to 18 carbon atoms and n is an integer greater than one.

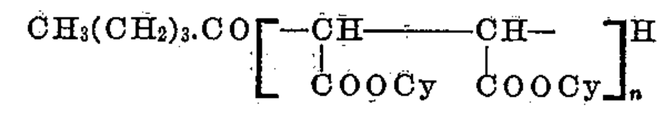
2. A hydrocarbon lubricant composition containing up to 1.0 per cent by weight, based on the total composition, of a liquid telomeric polyalkyl oxoester having the general formula



in which R is an alkyl radical of from 1 to 12

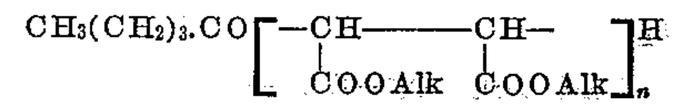
carbon atoms, and R′ and R″ are selected from the class consisting of alkyl, cycloalkyl, aryl, alkaryl and aralkyl radicals of from 1 to 18 carbon atoms and n is an integer greater than one.

3. A substantially antifoaming hydrocarbon lubricant composition containing up to 1.0 per cent by weight, based on the total composition, of a liquid telomer having the formula



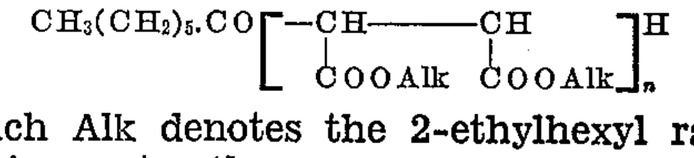
in which Cy denotes the cyclohexyl radical and n is an integer greater than one.

4. A substantially antifoaming hydrocarbon lubricant composition containing up to 1.0 per cent by weight, based on the total composition, of a liquid telomer having the formula



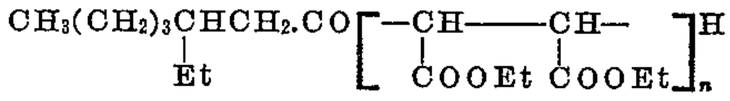
in which Alk denotes the 2-ethylhexyl radical and n is an integer greater than one.

5. A substantially antifoaming hydrocarbon lubricant composition containing up to 1.0 per cent by weight, based on the total composition, of a liquid telomer having the formula



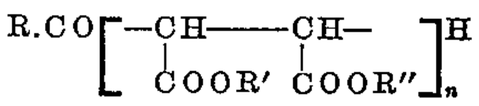
in which Alk denotes the 2-ethylhexyl radical and n is greater than one.

6. A substantially antifoaming hydrocarbon lubricant composition containing up to 1.0 per cent by weight, based on the total composition, of a liquid telomer having the formula



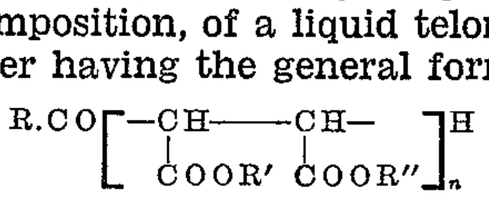
in which Et denotes the ethyl radical and n is an integer greater than one.

7. The method of imparting antifoaming properties to hydrocarbon oil compositions which comprises incorporating into said compositions up to 1.0 per cent by weight, based on the total composition, of a liquid telomeric polyalkyl oxoester having the general formula



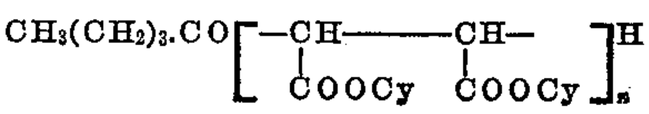
in which R is an alkyl radical of from 1 to 12 carbon atoms, and R′ and R″ are selected from the class consisting of alkyl, cycloalkyl, aryl, alkaryl and aralkyl radicals of from 1 to 18 carbon atoms and n is an integer greater than one.

8. The method of imparting antifoaming properties to hydrocarbon lubricant compositions which comprises incorporating into said composition up to 1.0 per cent by weight, based on the total composition, of a liquid telomeric polyalkyl oxoester having the general formula



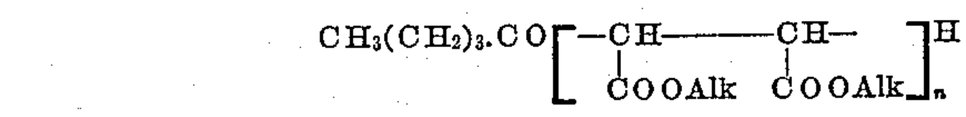
in which R is an alkyl radical of from 1 to 12 carbon atoms, and R′ and R″ are selected from the class consisting of alkyl, cycloalkyl, aryl, alkaryl and aralkyl radicals of from 1 to 18 carbon atoms and n is an integer greater than one.

9. The method of imparting antifoaming properties to hydrocarbon lubricant compositions which comprises incorporating into said compositions up to 1.0 per cent by weight, based on the total composition, of a liquid telomer having the formula



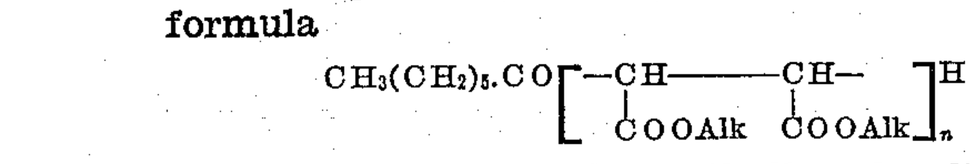
in which Cy denotes the cycloalkyl radical and n is an integer greater than one.

10. The method of imparting antifoaming properties to hydrocarbon lubricant compositions which comprises incorporating into said compositions up to 1.0 per cent by weight, based on the total composition, of a liquid telomer having the formula



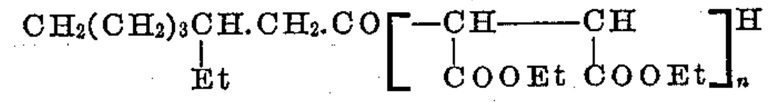
in which Alk denotes the 2-ethylhexyl radical and n is an integer greater than one.

11. The method of imparting antifoaming properties to hydrocarbon lubricant compositions which comprises incorporating into said compositions up to 1.0 per cent by weight, based on the total composition, of a liquid telomer having the formula



in which Alk denotes the 2-ethylhexyl radical and n is an integer greater than one.

12. The method of imparting antifoaming properties to hydrocarbon lubricant compositions which comprises incorporating into said compositions up to 1.0 per cent by weight, based on the total composition, of a liquid telomer having the formula



in which Et denotes the ethyl radical and n is an integer greater than one.

JOSEPH E. FIELDS.
TRACY M. PATRICK, JR.

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