Patented July 7, 1953

2,644,794

UNITED STATES PATENT OFFICE

2,644,794

HYDROCARBON OIL COMPOSITIONS

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No Drawing. Application November 15, 1950, Serial No. 195,898

3 Claims. (Cl. 252—52)

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This invention relates to anti-foaming hydrocarbon oils and deals more particularly with hydrocarbon oils containing small amounts of certain ketonic epoxide compounds as anti-foaming agents.

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 crankcase 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.

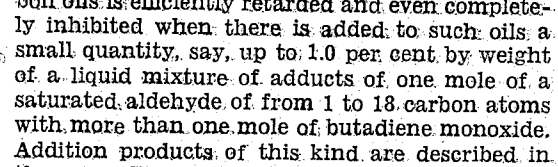
New developments in engine construction have constantly demanded lubricants having properties not possessed by crude hydrocarbon oils. Such properties are now generally conferred to lubricants by the use of additives. For example, in order to satisfy the lubrication requirements of hypoid gears, materials 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 formulation 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.

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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 anti-foam additives.

A number of anti-foam additives, i. e., anti-foaming 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 reactivity 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 I 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, up to 1.0 per cent by weight of a liquid mixture of adducts of one mole of a saturated aldehyde of from 1 to 18 carbon atoms with more than one mole of butadiene monoxide. Addition products of this kind are described in the copending application of Tracy M. Patrick, Jr., Serial No. 195,914 filed November 15, 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 17 carbon atoms and n is an integer of from 2 to 20.

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, n-caproic-aldehyde, isohexaldehyde, 2-ethylhexaldehyde, octaldehyde, capric aldehyde, undecaldehyde, lauric aldehyde, palmitic aldehyde, stearic aldehyde, etc.

The liquid mixture of adducts is obtainable by contacting butadiene monoxide with the saturated aldehyde in the presence of a free-radical liberating agent, e. g., a peroxidic compound as catalyst, allowing the resulting mixture to stand at ordinary or increased temperatures until formation of the liquid mixture of adducts has occurred, and removing from the resulting reaction product any initial unreacted material and 1:1 molar adduct. The residue is a liquid mixture of a series of adducts having the above formula.

The present aldehyde-butadiene oxide adducts are effective anti-foaming agents only 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 .05 per cent of the adducts is preferred, depending upon the nature of the oil. Heavy oils and oils containing foam-inducing adjuvants require more of the present anti-foaming adducts than do base oils of good viscosity characteristics.

The anti-foaming effect of the aldehyde-butadiene oxide adducts is not materially affected by the presence of other adjuvants in the oil. The present adducts are stable ketonic epoxides 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 additives in the oil has substantially no effect on the adducts. Hydrocarbon oils containing the present anti-foaming 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 anti-foaming effect of the aldehyde-butadiene oxide adducts is obtained only when they are employed in concentrations of up to 1.0% by weight, the adducts 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 adducts may be manufactured and sold for use as lubricant additives. Addition of small amounts of such concentrate to hydrocarbon oils may be made so as to supply an oil containing suitable quantities of the adducts.

Hydrocarbon oils which are rendered substantially anti-foaming by incorporation therein of quantities of up to 1.0 per cent of the present adducts 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 anti-foaming 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 was supplied at the rate of 0.2 cubic feet 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 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 was determined the anti-foaming effect of a liquid mixture of n-butyraldehyde-butadiene oxide adducts when added to a Champlin SAE base oil in concentrations of from 0.2% to 0.5% by weight of the oil. The liquid mixture of adducts, B. P. above 81° C./10 mm. consisted of adducts of one mole of n-butyraldehyde with from 2 to 20 moles of butadiene oxide and were prepared by maintaining at a temperature of about 74° C. for a time of 68.5 hours a mixture consisting of 216 g. (3.0 moles) of n-butyraldehyde, 70 g. (1.0 mole) of butadiene monoxide and 2.0 g. of benzoyl peroxide, and removing from the resulting reaction mixture material which boiled below 81° C./10 mm., as described in the previously cited copending application. The following results were obtained:

Concentration of adduct, weight percent	Foam
0.02	10 cc.
0.025	2 cc.
0.03	none
0.05	none

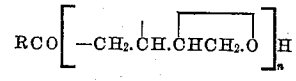
In the absence of an additive, the Champlin 30 SAE oil gave 71 cc. of foam under the same testing conditions.

Nonfoaming hydrocarbon oil compositions may

be obtained by incorporating into such oils in a quantity of up to 1.0% based on the weight of the composition, other liquid mixtures of adducts of one mole of a saturated, aliphatic aldehyde with from 2 to 20 moles of butadiene oxide. Thus, instead of the butyraldehyde-butadiene oxide adducts employed in the above example there may be used, e. g., adducts of one mole of acetaldehyde, of octaldehyde or of stearaldehyde, with from 2 to 20 moles of butadiene oxide. The present adducts impart anti-foaming properties to hydrocarbon oils, generally, in the presence or absence of other customarily employed additives such as extreme-pressure resisting additives, detergent additives, etc.

What I claim is:

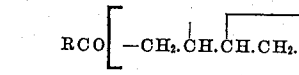
1. A substantially foam-resisting hydrocarbon oil composition containing up to 1.0 per cent by weight based on the weight of the composition of a liquid mixture of adducts having the formula



in which R is an alkyl radical of from 1–17 carbon atoms and n is an integer of from 2–20.

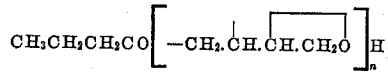
2. A lubricant composition containing a hydrocarbon oil and up to 1.0 per cent by weight

based on the weight of the composition of a liquid mixture of adducts having the formula



in which R is an alkyl radical of from 1–17 carbon atoms and n is an integer of from 2–20.

3. A lubricant composition containing a hydrocarbon oil and up to 1.0 per cent by weight based on the weight of the composition of a liquid mixture of adducts having the formula



in which n is an integer of from 2–20.

JOSEPH E. FIELDS.

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