

1

3,574,575

**LIQUID HYDROCARBON OIL COMPOSITIONS
CONTAINING ESTERS OF STYRENE-MALEIC
ANHYDRIDE COPOLYMERS AS FLUIDITY
IMPROVERS**

Paul Y. C. Gee, Woodbury, and Harry J. Andress, Jr.,
Pitman, N.J., assignors to Mobil Oil Corporation
No Drawing. Continuation-in-part of application Ser. No.
672,469, Oct. 3, 1967. This application Apr. 21, 1969,
Ser. No. 818,127

Int. Cl. C10I 1/18

U.S. Cl. 44—62

4 Claims

ABSTRACT OF THE DISCLOSURE

Liquid hydrocarbon oil compositions are provided which contain small amounts, sufficient to improve their fluidity characteristics, of esters of styrene-maleic anhydride copolymers having at least 20 carbon atoms in the alkyl portion. A method for preparing these esters is also provided.

**CROSS-REFERENCE TO RELATED
APPLICATIONS**

Continuation-in-part of application Ser. No. 672,469,
filed Oct. 3, 1967, now abandoned.

BACKGROUND OF THE INVENTION**(1) Field of the invention**

This invention, which is a continuation-in-part of our application Ser. No. 672,469, filed Oct. 3, 1967, and now abandoned, relates to improved liquid hydrocarbon compositions, and in one of its aspects, relates to liquid hydrocarbon compositions having improved fluidity characteristics. More particularly, in this aspect, the invention relates to liquid hydrocarbon compositions containing certain agents which are effective in functioning as pour point depressants and fluidity improvers, particularly in such liquid hydrocarbon compositions as crude oils and petroleum residual oils.

(2) Description of the prior art

Prior to the present invention, various materials have been suggested by the prior art as fluidity improvers in liquid hydrocarbons. In this respect, it has been found that such fluidity improvers have not proved entirely satisfactory with regard to improving the fluidity characteristics of liquid hydrocarbons where the hydrocarbons to be treated boil over a substantially wide range. Furthermore, some fluidity improvers have proved effective in certain types of oils, while exhibiting more limited improvement in other types. More specifically, the ability to employ a fluidity improver in liquid hydrocarbons which boil, for example, within the range from about 75° F. to about 1000° F. and which are also effective in various types of oils, for example, crude oils or petroleum residual oils, is most desirable.

SUMMARY OF THE INVENTION

It has now been found, as more fully hereinafter described, that liquid hydrocarbon compositions can be provided possessing improved fluidity characteristics by incorporating therein relatively small amounts of esters

2

of styrene-maleic anhydride copolymers having at least 20 carbon atoms in the alkyl portion. In accordance with the invention, these esters can be effectively employed in the liquid hydrocarbon compositions as pour point depressants and fluidity improvers in an amount from about .001 percent to about 1 percent, and preferably from about .01 percent to about 0.5 percent, by weight, of the total weight of the liquid hydrocarbon composition. Preferred esters are those which have from 20 to about 24 carbon atoms in the alkyl portion.

The liquid hydrocarbons improved in accordance with the present invention may comprise any hydrocarbons in which fluidity improvement is desirable. A field of specific applicability, in accordance with the present invention, is in the improvement of mineral oil compositions, for example, liquid hydrocarbons boiling at a temperature from about 75° F. to about 1000° F. Of particular importance is the treatment of petroleum distillate oils which have pour and flow points above about 75° F. and which boil as high as about 750° F. or higher. It should be noted, in this respect, that the term "distillate oils" is not intended to be restricted to straight-run distillate, catalytically or thermally cracked (including hydrocracked distillate oils) or mixtures of straight-run distillate oils, naphthas and the like, with cracked distillate stocks. Moreover, such oils can be treated in accordance with well known commercial methods, such as acid or caustic treatment, hydrogenation, solvent refining, clay treatment, and the like.

The distillate oils are characterized by their relatively low viscosity, pour point and the like. The principal property which characterizes these hydrocarbons, however, is their distillation range. As hereinbefore indicated, this range will preferably lie between about 75° F. and about 750° F. Obviously, the distillation range of each individual oil will cover a narrower boiling range falling, nevertheless, within the above mentioned limits. Likewise, each oil will boil substantially and continuously throughout its distillation range.

As hereinbefore indicated, the liquid hydrocarbon compositions improved in fluidity characteristics through the use of the ester copolymers of the present invention have broad applicability to liquid hydrocarbon compositions in the form of crude oils or petroleum residual oils. Thus, the fluidity characteristics of very high wax-containing petroleum residual oils, such as the residuum of North African crude oils designated as Zelden, or similar petroleum oils which boil above approximately 650° F. and have pour points above 75° F. have broad applicability. Another specific type of crude oil to which the present invention also has broad applicability is the Amal crudes.

As previously described, the novel fluidity improvers of the present invention comprise esters of styrene-maleic anhydride copolymers having at least 20 carbon atoms in the alkyl portion. In general, the polymerization reaction for producing the above-described copolymers is carried out at a temperature from about 50° C. to about 250° C., and preferably from about 100° C. to about 200° C., in the presence of an organic peroxide catalyst, for example, benzoyl peroxide or di-tertiary butyl peroxide, in an amount sufficient to permit polymerization to take place. Small amounts of the catalyst are usually sufficient for such purpose, for example, amounts from about 0.1

percent to about 10 percent, by weight, of the polymerization mixture. In preparing the ester copolymer, 1 mole of styrene and 1 mole of maleic anhydride are subjected to copolymerization. Thereafter, to the reaction mixture are added 1 or 2 moles of a saturated straight-chain alcohol having a minimum of 20 carbon atoms, which in the presence of an acid catalyst will result in esterification of the copolymer.

DESCRIPTION OF SPECIFIC EMBODIMENTS

The following data and examples will serve to illustrate the preparation of the novel ester copolymers of the present invention and their efficacy for improving the fluidity characteristics of liquid hydrocarbon compositions. It will be understood, however, that it is not intended the invention be limited to the particular ester copolymers or the particular liquid hydrocarbon compositions containing these ester copolymers, as described. Various modifications of these compositions, as previously indicated, can be employed and will be readily apparent to those skilled in the art.

Example 1.—Preparation of dibehenyl (docosanyl) ester of styrene-maleic anhydride copolymer

26 grams (0.25 mole) of styrene, 24.5 grams (0.25 mole) maleic anhydride, 0.5 gram of benzoyl peroxide and 200 grams of xylene as a diluent were stirred to a temperature of about 135° C. over a period of four hours. 165 grams (0.5 mole) of commercial grade behenyl alcohol and 7 grams of paratoluene sulfonic acid were then added to the reaction mixture, and the resulting mixture was stirred with refluxing to a temperature of about 200° C. The resulting product was found to comprise a dibehenyl (docosanyl) ester of styrene-maleic anhydride copolymer.

Example 2.—Preparation of dieicosanyl ester of styrene-maleic anhydride copolymer

26 grams (0.25 mole) of styrene, 24.5 grams (0.25 mole) of maleic anhydride, 0.5 gram of benzoyl peroxide and 200 grams of xylene as a diluent were stirred to a temperature of about 115° C. over a period of about four hours. 150 grams (0.5 mole) of commercial grade 1-eicosanol and 6 grams of paratoluene sulfonic acid were added to the reaction mixture, and the resulting mixture was stirred with refluxing to a temperature of about 220° C. The resulting product was found to comprise a dieicosanyl ester of styrene-maleic anhydride copolymer.

Example 3.—Preparation of didocosanyl ester of styrene-maleic anhydride copolymer

26 grams (0.25 mole) of styrene, 24.5 grams (0.25 mole) of maleic anhydride, 0.5 mole of benzoyl peroxide and 200 grams of xylene as a diluent were stirred to a temperature of about 118° C. over a period of about four hours. 165 grams (0.5 mole) of commercial grade 1-didocosanol and 6 grams of paratoluene sulfonic acid were added to the resulting reaction mixture and stirred with refluxing to a temperature of about 225° C. The resulting product was found to comprise a didocosanyl ester of styrene-maleic anhydride copolymer.

Example 4.—Preparation of ditetracosanyl ester of styrene-maleic anhydride copolymer

13 grams (0.125 mole) of styrene, 12.25 grams (0.125 mole) of maleic anhydride, 0.25 gram of benzoyl peroxide and 100 grams of xylene as a diluent were stirred to a temperature of about 100° C. over a period of about two hours. 88 grams (0.25 mole) of commercial grade 1-tetracosanol and 5 grams of paratoluene sulfonic acid were added to the resulting reaction mixture and stirred with refluxing to a temperature of about 215° C. The resulting product was found to comprise a ditetracosanyl ester of styrene-maleic anhydride copolymer.

Example 5.—Preparation of monobehenyl ester of styrene-maleic anhydride copolymer

26 grams (0.25 mole) of styrene, 24.5 grams (0.25 mole) of maleic anhydride, 0.5 gram of benzoyl peroxide and 200 grams of toluene as a diluent were stirred to a temperature of about 100° C. over a period of about three hours. 83 grams (0.25 mole) of commercial grade behenyl alcohol and 5 grams of paratoluene sulfonic acid were added to the resulting reaction mixture and stirred with refluxing to a temperature of about 205° C. The resulting product was found to comprise a monobehenyl ester of styrene-maleic anhydride copolymer.

The individual ester copolymers produced in accordance with the foregoing Examples 1 through 5 were next blended into an Amal crude oil and subjected to a series of tests for determining their efficacy as fluidity improvers. The Amal crude oil comprised a highly paraffinic, waxy, low sulfur, high asphaltene content crude oil from Libya in Africa. The same tests were also applied with respect to an Amal residual fuel oil for determining the efficacy of the present ester copolymers as fluidity improvers.

The ester copolymers of Examples 1 through 5, as hereinbefore described and having a minimum of 20 carbon atoms in the respective alkyl portions, were subjected to test method ASTM Test No. D-97 for determination of respective pour point. This test was applied against the uninhibited as well as against samples of the same oil containing the indicated concentrations of the respective ester copolymers produced in accordance with the foregoing Examples 1 through 5. The results obtained are shown in the following Table I.

TABLE I.—ASTM POUR TEST RESULTS
[ASTM Test Number D-97]

	Concentration, percent weight	Pour point ° F.
Uninhibited crude oil	0	65
Uninhibited crude oil plus Example 1	0.06	30
Uninhibited crude oil plus Example 2	0.06	35
Uninhibited crude oil plus Example 3	0.06	25
Uninhibited crude oil	0	70
Uninhibited crude oil plus Example 4	0.06	25
Uninhibited crude oil plus Example 5	0.10	35
Uninhibited residual oil	0	100
Uninhibited residual oil plus Example 1	0.10	65
Uninhibited residual oil plus Example 2	0.10	85
Uninhibited residual oil plus Example 3	0.10	75
Uninhibited residual oil plus Example 4	0.10	75
Uninhibited residual oil plus Example 5	0.50	80

It will be apparent from the data set forth in the foregoing Table I that the ester copolymers of the present invention are highly effective as fluidity improvers in liquid hydrocarbons. As will be understood, results will vary with respect to the specific ester copolymers employed. In order to accomplish any given improvement, many of the aforementioned ester copolymers can be employed in very small amounts. Others can be effectively employed at the aforementioned practical concentrations of from about .01 to about 0.5 percent, by weight, of the liquid hydrocarbon composition.

For purposes of comparison in demonstrating the aforementioned criticality of the chain length of the ester employed for the preparation of the ester copolymers of the present invention which contain at least 20 carbon atoms in the alkyl portion, the di-1-octadecyl ester of styrene-maleic anhydride copolymer was individually blended in individual samples of the aforementioned Amal crude and residual oils, and also subjected to the aforementioned ASTM D-97 pour test and compared against the uninhibited oil. It was found that no significant improvement in pour point was realized. From the foregoing, it will be apparent that no significant improvement in fluidity characteristics as demonstrated by the respective pour point data is achieved by employing ester styrene-maleic anhydride copolymers which contain less than 20 carbon atoms in the respective alkyl portions.

To further demonstrate the efficacy of the novel ester copolymers of the present invention as fluidity improvers in liquid hydrocarbons, the individual ester copolymers were next blended into an Amal crude oil of the type hereinbefore described, and subjected to a series of tests for determination of fluidity characteristics by an evaluation of constant shear rates (94 secs.⁻¹) at 40° F. This test involves the use of a Ferranti-Shirley viscometer in which the cone is set on a plate sufficiently close to make electrical contact. The cone is rotated at a preset speed of 5 r.p.m., and the torque required to maintain this speed is recorded as a function of time. This test was applied against the uninhibited as well as against samples of the same oil containing the indicated concentrations of the respective ester copolymers produced in accordance with the foregoing Examples 1 through 5. The results obtained are shown in the following Table II.

TABLE II

[Constant Shear Rate (94 secs.⁻¹) Test Evaluation at 40° F. of Additives Blended in Amal Crude Oil]

Additive	Concentration percent weight	Peak shear stress, dynes/cm. ²	Viscosity after 100 seconds, shear, poise
Uninhibited crude oil.....	0.00	2,550	9.1
Uninhibited crude oil plus Example 1.....	0.06	612	3.2
Do.....	0.00	3,050	8.3
Uninhibited crude oil plus Example 2.....	0.06	758	4.4
Uninhibited crude oil plus Example 3.....	0.06	880	5.0
Uninhibited crude oil.....	0.00	3,480	8.3
Uninhibited crude oil plus Example 4.....	0.06	663	4.5
Uninhibited crude oil plus Example 5.....	0.06	1,823	7.7

It will be apparent from the data set forth in the foregoing Table II that the ester copolymers of the present invention are highly effective as fluidity improvers in liquid hydrocarbons on the basis of constant shear rate evaluations.

For purposes of comparison in demonstrating the aforementioned criticality of the chain length of the ester employed for the preparation of the ester copolymers of the present invention which contain at least 20 carbon atoms in the alkyl portion, the di-1-octadecyl ester of styrene-maleic anhydride copolymer was individually blended in another sample of the aforementioned Amal crude oil, and also subjected to the aforementioned constant shear rate test and compared against the uninhibited oil. It was found that no significant improvement in fluidity characteristics was realized. From the foregoing, it will be apparent that no significant improvement in fluidity characteristics as demonstrated by the respective constant shear rate evaluations is achieved by employing ester styrene-maleic anhydride copolymers which contain less than 20 carbon atoms in the respective alkyl portions.

As hereinbefore described, the mineral oil compositions of the present invention contain, as fluidity improvers, esters of a styrene-maleic anhydride copolymer having at least 20 carbon atoms in the alkyl portion. In this respect, the prior art has heretofore suggested the incorporation of copolymers of styrene and maleic acid esters as additives for lubricating compositions. In this regard, the following comparative data were obtained which will serve to establish that these respective copolymeric materials are not identical and that superior fluidity improvement properties are realized in employing the esters of styrene maleic anhydride copolymers of the present invention over copolymers of styrene and maleic acid esters as were heretofore employed.

Example 6—Preparation of styrene-dibehenyl maleate copolymer

A mixture of 74 grams (0.1 mole) of dibehenyl maleate, 10.4 grams (0.1 mole) of styrene, and 3.4 grams of diter-

tiary butyl peroxide was stirred at a temperature of about 150° C. for a period of about 20 hours. The resulting viscous product was found to comprise a styrene-dibehenyl maleate copolymer.

The ester copolymer of Example 1 and the styrene-dibehenyl maleate copolymer of Example 6, were subjected to the aforementioned test method ASTM Test No. D-97 for a comparative determination of respective pour points. This test was applied against an uninhibited as well as against samples of the same oil containing the indicated concentrations of the respective ester copolymer produced in accordance with the foregoing Example 1 and the styrene-dibehenyl maleate copolymer produced in accordance with the foregoing Example 6.

TABLE III.—ASTM POUR TEST RESULTS

[ASTM Test Number D-97]

	Concentration, percent weight	Pour point, ° F.
Uninhibited Amal crude oil.....	0.	65
Uninhibited Amal crude oil plus Example 1.....	0.01	40
Uninhibited Amal crude oil plus Example 6.....	0.01	55
Uninhibited Amal residual fuel oil.....	0.	100
Uninhibited Amal residual fuel oil plus Example 1.....	0.10	65
Uninhibited Amal residual fuel oil plus Example 6.....	0.10	85

It will be apparent from the comparative data set forth above that the ester copolymers of the present invention—e.g. the dibehenyl (docosanyl) ester of styrene-maleic anhydride copolymer—are superior for fluidity improvement in liquid hydrocarbon compositions over the styrene-dibehenyl copolymers of the prior art.

To further demonstrate the superiority of the ester copolymers of the present invention over the styrene-dibehenyl maleate copolymers of the prior art, the respective copolymeric materials were next blended into an Amal crude oil of the type hereinbefore described and subjected to the aforementioned test for determination of fluidity characteristics by an evaluation of constant shear rates. The comparative results obtained are shown in the following Table IV.

TABLE IV

[Constant Shear Rate (94 seconds.⁻¹) Test Evaluation at 40° F. of Additives Blended in Amal Crude Oil]

	Concentration percent weight	Viscosity after 100 seconds, shear, poise
Uninhibited Amal crude oil.....	0.00	9.1
Uninhibited Amal crude oil plus Example 1.....	0.06	3.2
Uninhibited Amal crude oil plus Example 6.....	0.06	5.2

It will be apparent from the data set forth in the foregoing Table IV that the ester copolymers of the present invention are superior as fluidity improvers in liquid hydrocarbons over the styrene-dibehenyl maleate copolymers of the prior art, on the basis of constant shear rate evaluation.

Although the present invention has been described with preferred embodiments, it will be understood that various modifications and adaptations thereof may be resorted to without departing from the spirit and scope of the invention, and that the liquid hydrocarbon compositions herein described may also contain other additive materials intended to enhance the value of such compositions in certain well-defined and specific aspects.

We claim:

1. A liquid hydrocarbon oil composition selected from the groups consisting of crude oil and residual oil, containing a small amount, sufficient to improve its pour point, of an alkyl ester of styrene-maleic anhydride copolymer having at least 20 carbon atoms in the alkyl portion, said styrene-maleic anhydride copolymer having been prepared by reacting styrene and maleic anhydride in a mol ratio of 1:1 and the alkyl ester of said copolymer having been prepared by reacting an alkanol and the

styrene-maleic anhydride copolymer in a mol ratio of from 1:1 to 2:1.

2. A composition as defined in claim 1 wherein said ester is present in an amount from about .001 percent to about 1 percent, by weight.

3. A composition as defined in claim 1 wherein said ester is present in an amount from about .01 percent to about 0.5 percent, by weight.

4. A composition as defined in claim 1 wherein said ester has from 20 to 24 carbon atoms in the alkyl portion. 10 44—70

References Cited**UNITED STATES PATENTS**

2,978,395 4/1961 Hollyday et al. ----- 252—56D

5 DANIEL E. WYMAN, Primary Examiner

W. J. SHINE, Assistant Examiner

U.S. Cl. X.R.