

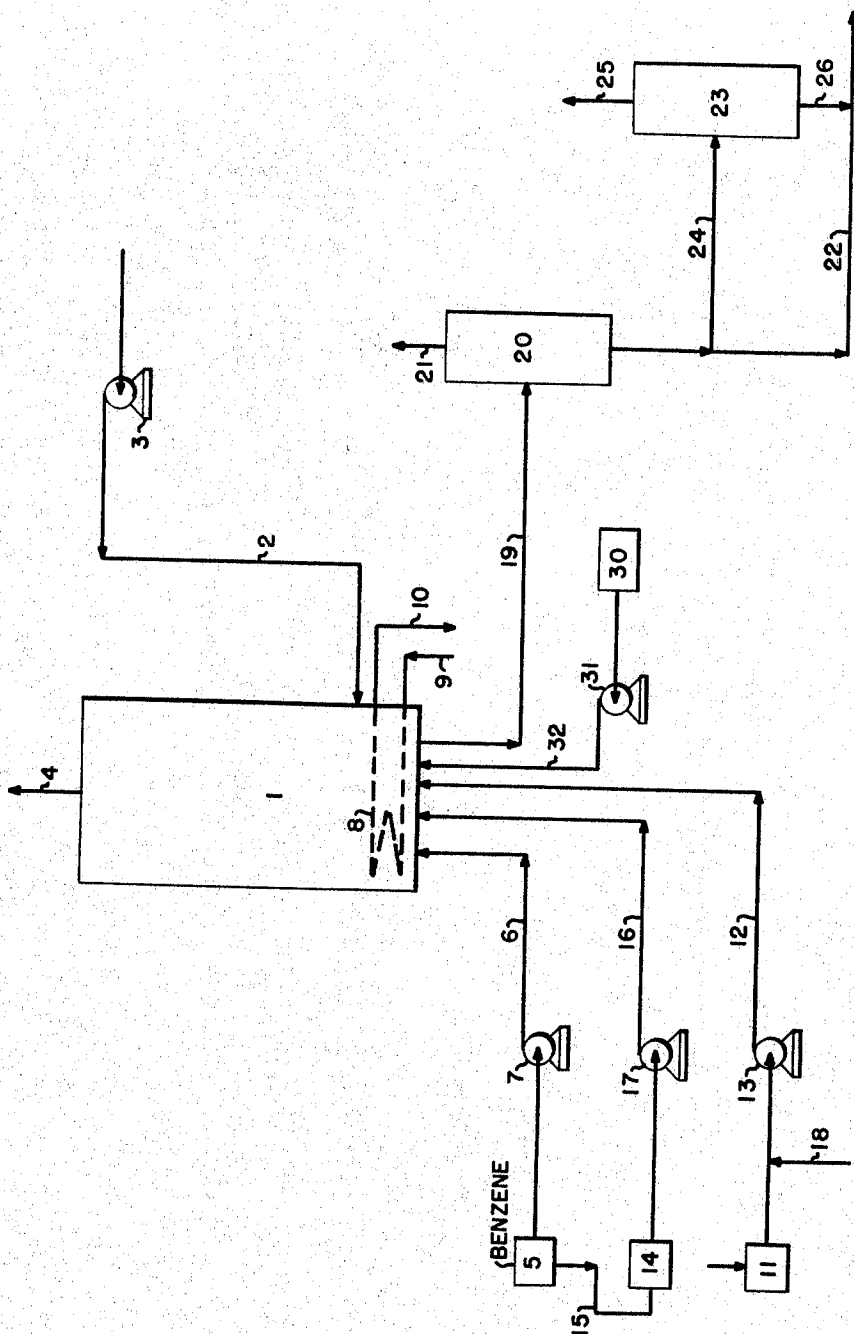
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TERPOLYMER POUR POINT DEPRESSANT AND METHOD OF MANUFACTURE

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TERPOLYMER POUR POINT DEPRESSANT AND METHOD OF MANUFACTURE

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This application is a continuation-in-part of Ser. No. 297,036 filed July 23, 1963, now abandoned.

The present invention is concerned with an improved terpolymer pour point depressant and with its method of manufacture. The terpolymer of the present invention is particularly effective for use with middle distillates. The pour depressant of the present invention comprises a terpolymer of ethylene, an alkyl fumarate or maleate and an olefinically unsaturated aliphatic ester containing from about 3 to 5 carbon atoms per molecule. The terpolymers of desirable molecular weights are obtained by controlling the conditions of the reaction. A particularly preferred terpolymer of the present invention is a terpolymer of ethylene, vinyl acetate and dilauryl fumarate.

With the increase in the use of hydrocarbon fuels of all kinds, serious problems have arisen in areas frequently subjected to low temperatures in the cold test characteristics of fuel. Particularly serious problems have been encountered with heating oils and diesel and jet fuels that have too high a pour point, resulting either in distributional or operating difficulties or both. For example, the distribution of heating oils by pumping or syphoning is rendered difficult or impossible at temperatures around or below the pour point of the oil. Furthermore, the flow of the oil at such temperatures through the filters is not maintained, leading to equipment failures.

Also, the low temperature properties of petroleum distillate fuels boiling in the range between about 250° and about 750° F. have attracted increasing attention in recent years because of the growth of market for such fuels in subarctic areas and because of the development of turbo-jet aircraft capable of operating at altitudes where temperatures of —50° F. or lower are encountered.

It is, therefore, an object of the present invention to utilize an improved terpolymer and describe its method of manufacture. These terpolymers are particularly effective pour depressants for middle distillates and lighter oils. In general, these oils boil in the range from about 250° and 750° F.

It is a still further object of the present invention to provide heating oils, diesel fuel oils, kerosenes and jet fuels having low pour points. Aviation turbo-jet fuels in which the polymers may be used normally boil between about 250° and about 550° F. and are used in both military and civilian aircraft. Such fuels are more fully defined by U.S. Military Specifications MIL-F-5624C, MIL-F-25554A, MIL-F-25558A, and amendments thereto. Kerosenes and heating oils will normally have boiling ranges between about 300° and about 750° F. and are more fully described in ASTM Specification D-396-48T and supplements thereto, where they are referred to as No. 1 and No. 2 fuel oils. Diesel fuels in which the polymers may be employed are described in detail in ASTM Specification D-975-53T and later versions of the same specification.

In accordance with the present invention the use of ethylene monomer in the propagation reaction for preparing the terpolymers herein is critical. The amount of ethylene present in the polymer should vary in the range from about 30 to 85 wt. percent, preferably from about 55 to 70 wt. percent, as for example 60 wt. percent.

Esters of ethylenedicarboxylic acid employed as the second constituent of the terpolymers are alkyl esters of

fumaric and maleic acids having esterifying groups containing from 1 to about 24 carbon atoms. Alkyl esters in which the alkyl groups contain from about 4 to about 18 carbon atoms are particularly useful because of the solubility properties which they impart to the terpolymers, and are therefore preferred for the purposes of the invention. In addition, the esters may be mono or dialkyl esters, but it is preferred, however, that they be dialkyl esters. The amount of fumarate or maleate present in the terpolymer should be in the range of from about 5 to 30 wt. percent, preferably from about 10 to 20 wt. percent as, for example, 15 wt. percent. Examples of such esters which may be employed to prepare the terpolymers include dibutyl fumarate, di-n-hexyl fumarate, dilauryl maleate, dilauryl fumarate, monohexadecyl fumarate, dioctadecyl maleate, di-2-ethyl-hexyl maleate, distearyl fumarate, dicetyl fumarate and the like.

Esters of fumaric or maleic acids prepared from commercial mixed alcohols may also be used in preparing the terpolymers employed in accordance with the invention. Such mixed alcohols include those prepared by the hydrogenation of coconut oil and marketed commercially under the trade name "Lorol." One such mixture of alcohols consists primarily of lauryl alcohols but contains compounds of from about 10 to about 18 carbon atoms per molecule. This particular "Lorol" alcohol normally contains about 4.0% of C₁₀ alcohol, about 55.5% of C₁₂ alcohol, about 22.5% of C₁₄ alcohol, about 14.0% of C₁₆ alcohol, and about 4.0% of C₁₈ alcohol. Tallow alcohol is a similar mixed product consisting primarily of cetyl and stearyl alcohols derived from tallow fat by saponification. Other mixed alcohols available commercially are derived from soybean oil, cotton seed oil, and similar natural products and also have chain lengths within the range recited above which render them suitable for purposes of the invention.

A still further class of alcohols which may be employed in preparing the esters used as monomers in accordance with the inventions are the oxo alcohols which are derived by the oxonation and hydrogenation of olefins. A variety of alcohols may be produced by this method, depending upon the particular olefins employed. If a C₇ olefin derived from propylene and butylene is used, for example, C₈ oxo alcohol is produced. Typically, C₈ oxo alcohol consists of 29% of 3,5-dimethyl hexanol, 25% of 4,5-dimethyl hexanol, 17% of 3,4-dimethyl hexanol, 16% of 4-methylheptanol and 5-methyl heptanol, 2.3% of 4-ethyl hexanol, 1.4% of 5,5-dimethyl hexanol, 4.3% of 2-alkyl-alkynols, and 5% of other alcohols. If a propylene tetramer is subjected to oxonation and subsequent hydrogenation, a C₁₃ oxo alcohol is produced. This higher alcohol also consists of a mixture of alcohols similar to the C₈ oxo alcohol mixture. Other alcohols of different chain lengths and different degrees of branching may be produced in an analogous manner. All of these alcohols are suitable for use in forming the esters employed as one of the monomers of the additives of the invention.

The third monomer which is useful for polymerization with the aforescribed monomers include the olefinically unsaturated aliphatic esters containing from about 3 to 5 carbon atoms per molecule. In general, these compounds may comprise vinyl acetate, vinyl propionate, methyl methacrylate, and the like. The amount of C₃—C₅ unsaturated ester present in the terpolymer is within the range between about 10 to 40 wt. percent, preferably from about 20 to 30 wt. percent as, for example, 25 wt. percent.

The molecular weight of the terpolymer is critical and should be in the range from about 1,000 to 4,000, preferably in the range from 1,500 to 3,000, such as about 2,500. The molecular weights are determined in phenanthrene by K. Rast's method (Ber. 55, 1051, 3727 (1922)).

The terpolymer as described above is used in a concentration in the range from about .001 to 0.09% by weight, preferably in a concentration in the range from about 0.01 to 0.05% by weight.

The polymerization process employed to produce the terpolymer of the present invention is conducted in a typical hydrocarbon polymerization solvent as, for example, toluene, hexane, cyclohexane, n-heptane, isobutyl alcohol and the like. It is preferred, however, to use a benzene solvent.

The initiator comprises any conventional peroxide type catalyst such as benzoyl peroxide, tert-butyl hydroperoxide, di-tert-butyl peroxide, cumene peroxide and the like. Di-tert-butyl peroxide in varying amounts (e.g., 0.01-2.0 wt. percent based on reactants) was found to be particularly effective in promoting the polymerization.

The temperature of the polymerization reaction is in the range from about 250° to 350° F., preferably from 275° to 325° F. A very desirable temperature is about 300° F. The pressure is in the range from about 500 to 1,500 pounds, preferably 800 or 900 pounds.

For example, the autoclave or similar equipment containing the solvent, initiator, dilauryl fumarate and vinyl acetate is purged with nitrogen, then with ethylene before charging with a sufficient amount of ethylene to yield the desired pressure when heated to the reaction temperature. During the polymerization, additional ethylene is added to maintain the pressure at the desired level. The polymerization time may vary widely, e.g., from about 1 to about 30 hours. Polymerization is considered complete when the pressure drops less than 50 p.s.i.g. per hour. The product is stripped free of solvent, dilauryl fumarate and unreacted vinyl acetate under vacuum.

The present invention may be more fully understood by reference to the drawing illustrating one embodiment of the same. Referring specifically to the drawing, reactor 1 is first purged with nitrogen, introduced by means of line 2 and pump 3. Reactor 1 is then purged with ethylene which is introduced by means of line 2 and pump 3. Gases are removed from reactor 1 by means of line 4. The reactor is maintained at a positive pressure in the range from about 50 to 100 pounds absolute.

Approximately 1,400 parts by volume of benzene is introduced into reactor 1 from benzene storage 5 by means of line 6 and pump 7. Reactor 1 is then raised to a temperature of about 300° F. by means of heating element 8 wherein a heating fluid or equivalent means is introduced by means of line 9 and withdrawn by means of line 10. Reactor 1 is held at about 300° F. during the course of the reaction by the removal of heat or by the addition of heat thereto by suitable means. Ethylene is introduced by means of line 2 so as to raise the pressure of the reactor to about 900 pounds per square inch absolute.

The addition of vinyl acetate, dilauryl fumarate, and of di-tertiary-butyl-peroxide is started concurrently. It is also possible to stage the addition of the two esters in either order. The mixture of vinyl acetate and dilauryl fumarate is withdrawn from storage zone 11 and introduced into the reactor by means of line 12 and pump 13. Approximately 215 parts by volume of vinyl acetate mixed with for example 105 parts by volume of dilauryl fumarate are added over a four hour period. The peroxide is introduced by passing benzene into storage zone 14 by means of line 15 and then introducing the solution into the reactor 1 by means of line 16 and pump 17. Approximately 15 parts by volume of peroxide are combined with 45 parts by volume of benzene. The resulting 60 parts by volume of 25% peroxide solution in benzene is added to reactor 1 over a three to five hour period.

After the addition of the peroxide has been completed, the reactor is held for an additional one to two hours at a temperature of about 300° F. The ethylene is added continuously so as to maintain the pressure at about 900 pounds.

At the end of the reaction, the reactor is allowed to cool to about 160° F. and the reaction product is withdrawn by means of line 19 and passed into separation zone 20. Excess ethylene is removed overhead from separation zone 20 by means of line 21. The polymer product comprising the terpolymer in a benzene solution may be withdrawn by means of line 22 and further handled as desired. Under certain instances, it may be desirable to separate at least a portion of the benzene from the terpolymer. Under these conditions, the benzene-terpolymer mixture is passed to stripper 23 by means of line 24. Benzene is removed overhead by means of line 25, while a terpolymer product is withdrawn by means of line 26. Under certain conditions, the dilauryl fumarate may be introduced by means of line 18 and the vinyl acetate from zone 11. Also, the dilauryl fumarate may be introduced directly into zone 1 from zone 30 by means of pump 31 and line 32.

The quantities mentioned above may be varied under certain conditions. For example, based upon 1,000 parts by weight of benzene, the amount of vinyl acetate may be varied from about 100 to 250 parts by weight, and the dilauryl fumarate and ethylene added in concentrations specified heretofore based upon the amount of vinyl acetate utilized.

The pour depressants of the instant invention are found compatible with other additive materials and may be blended successfully with petroleum oils containing minor amounts of viscosity index improvers, rust inhibitors, oiliness agents, oxidation inhibitors, and the like.

Example 1

In order to further illustrate the invention, a number of operations were conducted in accordance with the above described technique. The results of these operations are illustrated in Table I wherein it is seen that the terpolymers of the instant invention are very effective pour point depressants.

TABLE I.—TERPOLYMERS OF ETHYLENE-VINYL ACETATE—DILAURYL FUMARATE POUR DEPRESSANTS FOR MIDDLE DISTILLATE GAS OILS
[Conditions of synthesis: about 1,400 ml. of benzene as solvent, ethylene pressure to maintain 900 p.s.i.g., temperature 275° F., 6 hours reaction time]

Conditions.....	A	B	C	D	E
Vinyl acetate, g.....	200	200	200	200	200
Injection period, hours.....	4	4	(3)	(4)	4
Dilauryl fumarate, g.....	52.5	105	105	105	105
Injection period, hours.....	4	4	(3)	3	(4)
Di-t-butyl peroxide, g.....	11.9	11.9	11.9	11.9	11.9
Injection period, hours.....	4	4	5	5	4
Product:					
Yield, g.....	535	420	462	555	495
Sap. No.....	200.0	214	216.5	236.7	186
Mol. Wt. ¹	2,040	2,700	2,900	3,180	2,800
Pour Depressing Potency, ° F. ²					
At 0.015 wt. percent.....	75	80	75	70	70
At 0.025 wt. percent.....	85	85	85	80	80

¹ Cryoscopically in phenanthrene.

² In Reference Oil, 50/50 blend of virgin and cracked gas oils; ASTM pour, +25° F.; boiling range, 350° to 625° F.

³ Over 2 hrs.

⁴ At Start.

⁵ Over 3 hrs. after V.A.

It is not intended that this invention be limited to the specific examples presented by way of illustration. The scope of the invention is limited only by the appended claims.

What is claimed is:

1. A hydrocarbon composition having improved pour characteristics which comprises a major proportion of a petroleum distillate fuel boiling within the range between about 250° F. and 750° F. and a pour depressing effective amount of an oil soluble terpolymer consisting essentially of from about 30 to 85 wt. percent of ethylene, from about 10 to 40 wt. percent of an olefinically unsaturated C₃-C₅ monocarboxylic ester and from about 5 to 30 wt. percent of an ester of ethylenedicarboxylic acid and a C₁-C₂₄ monohydric alcohol; said terpolymer hav-

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ing a molecular weight in the range of from about 1,000 to 4,000.

2. A composition as defined by claim 1 wherein said olefinically unsaturated C₃-C₅ monocarboxylic ester is vinyl acetate.

3. A composition as defined by claim 2 wherein said ester of ethylenedicarboxylic acid is a C₄-C₁₈ dialkyl fumarate.

4. A composition as defined by claim 3 wherein the molecular weight of said terpolymer is within the range between about 1,500 to 3,000.

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