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3,069,245

SYNERGISTIC MIXTURE OF POUR DEPRESSANTS FOR MIDDLE DISTILLATES

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The present invention is concerned with improving the flow of fuels at low temperatures and improving pour point characteristics of middle distillates. More particularly, the invention relates to the preparation of improved low cold test hydrocarbon fuels, in particular heating oils and diesel fuels, kerosene, aviation turbo-jet fuels, and other fuels that are subject to low temperatures. The preferred class of pour depressants of the present invention are synergistic mixtures of pour depressants, which mixtures comprise in combination an acylated polystyrene used in conjunction with a pour depressant selected from the class consisting of an alkylated polystyrene and copolymer of ethylene and vinyl acetate.

With the increase in the use of hydrocarbon fuels of all kinds, a serious problem has arisen in areas frequently subject to low temperatures in the cold test characteristics of fuels. Particularly, serious problems have been encountered by 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 cannot be maintained, leading to the failure of the equipment to operate.

It is, of course, well known to add pour depressants to lubricating oils to lower the pour point. These lube oil additives, mostly high molecular weight organic compositions formed by alkylation of benzene or naphthalene or derivatives thereof or by polymerization of lower molecular weight methacrylates, or by condensation polymerization of various kinds, are not satisfactory in service with middle distillate and lighter fuels. Poor performance of these additives might possibly result from the structural differences between waxes occurring in lubricating oils and so-called middle distillates.

A wide variety of compounds have been found to be effective as pour point depressants for lubricating oil. Among the best known are "Parafflow," "Santopour," and "Acryloid" and their modifications. They are prepared either by condensing aromatic compounds with long chain paraffins, such as wax, or by condensing olefinic esters. It is generally considered that these pour depressants are effective in that in cooling an additive-containing oil, the hydrocarbon chain of the additive becomes incorporated into the crystal lattice of the separated wax, while the other part of the pour depressant molecule prevents the crystals from adhering together to form a gel structure. The failure of these additives to be effective in middle distillates may at least in part be due to the basic difference in the composition between the wax in lubricating oils and that in middle distillate fuels.

It is, therefore, the principal object of the present invention to set forth an improved pour depressant for middle distillate and lighter fuels. The boiling ranges of these oils are generally about 250° to 750° F.

The petroleum distillate fuels in which the additive materials of the invention are employed consist of a major proportion, at least 95%, of liquid hydrocarbons boiling at temperatures between about 70° F. and about 750° F. These fuels include gasolines such as aviation,

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marine and automotive or motor gasolines, aviation turbo-jet fuels such as JP-1, JP-4 and JP-5 fuels, and diesel fuels such as marine, stationary and automotive diesel engine fuels.

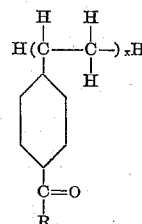
Aviation turbo-jet fuel consists of at least 95% of a mixture of volatile hydrocarbons. It is defined by U.S. Military Specifications MIL-F-5616 and MIL-F-5624C. Its volatility is such that its end point does not exceed 572° F. Its viscosity is between 0.5 and 1.5 centistokes at 100° F.

Diesel fuels as referred to in connection with the invention consist of at least 95% of a mixture of hydrocarbons boiling between 250° F. and 750° F. either by ASTM Method D86-56 when their end points do not exceed 600° F. or by ASTM Method D-158-54. Diesel fuels are defined by ASTM Specification D-975-53T and fall into grades 1D, 2D and 4D, in all of which the additive materials of the invention may be used. They have viscosities between 1.4 and 26.4 centistokes.

The liquid fuels in which the additive materials may be incorporated thus comprise at least 95% by weight of a mixture of hydrocarbons having a boiling range between the limits of 75° F. and 750° F. and a viscosity between the limits of 0.264 and 26.4 centistokes at 100° F.

In accordance with the present invention, a synergistic mixture is used which comprises an acylated polystyrene used in conjunction with a material selected from the class consisting of an alkylated polystyrene and a copolymer of ethylene and vinyl acetate.

The acylated polystyrene of the present invention used in conjunction with the alkylated polystyrene or the copolymer of ethylene and vinyl acetate are prepared with said fatty acid chlorides of critical composition and themselves are active pour depressants for middle distillates. The acylates of interest have the following structure:



where the acyl group



is defined according to the "contributory number" table and R is normally a straight chain alkyl group of about C₇ to C₁₅, and x is a number from 3 to 20.

In general, the method of acylation may vary appreciably. The methods which are disclosed in U.S. Patent No. 2,703,817 entitled "Process for the Preparation of Lubricating Oil Additives," inventor: George E. Serniuk, and in U.S. Patent No. 2,500,082 entitled "Acylated Derivatives of High Molecular Weight Copolymers," inventors: Eugene Lieber and William H. Smyers, may be utilized.

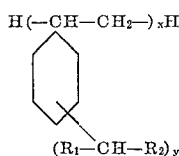
Broadly, the method of acylation comprises dissolving the polystyrene in a suitable solvent, such as chlorobenzene, o-dichlorobenzene, or tetra chloro-ethylene and adding to the solution the equimolar carboxylic acid chloride/aluminum chloride complex at temperatures of 30° to 70° C. (preferably 40° to 60° C.), with provision for carrying away the evolved hydrogen chloride. After all the acid chloride/aluminum chloride complex has been added (one mole per mole of phenyl groups in the polystyrene, plus a slight excess) and hydrogen chloride evolution has stopped, the catalyst is destroyed with water or

alcohol, the acylate is taken up in a suitable solvent, such as heptane or kerosene and washed with water and alkaline solutions. The resinous product may be isolated as the pure material by evaporating all solvents, or it may be used in solution for making blends in middle distillates.

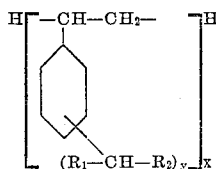
For obtaining the superior pour point depressants of this invention, it is desired that the polystyrene starting material have an intrinsic viscosity within a range of about 0.2 to 2.0, preferably 0.8 to 1.5. These viscosities correspond to molecular weights within a range of from about 10,000 to 75,000, preferably 30,000 to 60,000 Staudinger (if the constant for isobutylene polymers is assumed to apply). Since the amounts of the other reactants are based on the weight of the polystyrene, the amount of polystyrene used will depend upon restrictions such as equipment capacity, etc. The cryoscopic molecular weight after acylation was about 700 to 5,000; the intrinsic viscosity about 0.1 to 0.5. The 700 molecular weight comprises, in essence, a trimer containing three acylated phenyl groups, whereas, the 5,000 molecular weight comprises, in essence, about 18 acylated phenyl groups, on the average, per polymer molecule.

The acylating agent chosen for the preparation of the improved pour point depressants of this invention will be aliphatic in nature and will preferably contain from 8 to 16 carbon atoms in a straight chain. Although C_8 , C_{10} , C_{12} , C_{14} and C_{16} acid chlorides are used in the examples specifically detailing the instant invention, any straight chain acid chlorides having the above requirements may be used. It is preferred that equimolar quantities of polystyrene and the acylating agent be used; however, from 0.80 to 1.20 mols of acylating agent per mol equivalent of polystyrene is operable. A large excess of acylating agents does no harm, but it does not react and so is wasted.

The acylated polystyrene as described above is used in conjunction with either an alkylated polystyrene or with a copolymer of ethylene and vinyl acetate. The alkylated polystyrene compounds are prepared with certain olefins and have a critical composition. The olefin should have a molecular weight in the range 200 to 250 and if it is a mixture at least 95 mole percent of the olefins should have molecular weights individually in the range of 170 to 280. The alkylates of interest have the following structure:



or



R_1 is an alkyl group, straight or branched, containing 9 carbon atoms or less while R_2 is a straight-chain alkyl group containing 10 carbon atoms or more, x is the number from 3 to 15 inclusive and y is 0.75 to 2.00.

All products were made under the reaction conditions of solvent, temperature, catalyst and finishing procedure as described in U.S. Patent No. 2,756,265 assigned to Esso Research and Engineering Company, entitled "Alkylated Polystyrene Pour Depressants," inventor: William C. Hollyday, Jr.

Broadly, the process comprises the steps of dissolving the desired polystyrene in an inert solvent and heating the mixture until the polystyrene is completely in solu-

tion. The mixture is then cooled to the desired reaction temperature at which time the nitrobenzene and the Friedel-Crafts catalyst is added. The alkylating agent is then added dropwise and the reaction temperature selected is maintained by cooling or heating as necessary. After the completion of the reaction, the alkylates are purified by well known techniques, among which is precipitation with methanol, dissolving in hexane and reprecipitating several times with methanol or isopropanol. If desired, the alkylated material may be dissolved in oil, washed with alkaline solutions, and the oil solution then steam stripped to result in the final product.

For obtaining the superior pour point depressants of this invention, it is desired that the polystyrene starting material have an intrinsic viscosity within a range of about 0.2 to 1.0, preferably 0.8 to 1.5. These viscosities correspond to molecular weights within a range from about 10,000 to 75,000, preferably 30,000 to 60,000 Staudinger. Since the amounts of the other reactants are based on the weight of the polystyrene, the amount of polystyrene used will depend upon restrictions such as equipment capacity, etc. The cryoscopic molecular weight after alkylation was about 700 to 3,000; the intrinsic viscosity about 0.1 to 0.5. The 700 molecular weight comprises, in essence, a trimer containing three alkylated phenyl groups, whereas the 3,000 molecular weight comprises, in essence, about eight alkylated phenyl groups.

The alkylation agent chosen for the preparation of the improved pour point depressants of this invention will be olefinic in nature and will preferably contain from 12 to 18 carbon atoms in a straight chain. Although dodecene-1 through eicosylene and cracked wax are used, any olefinic material having the above requirements may be used. It is preferred that equimolar quantities of polystyrene and the alkylating agent be used, however, from 0.80 to 2.00 mols of alkylation agent per mol equivalent of polystyrene is operable.

These alkylated polystyrenes should be prepared where the olefin mixture has a molecular weight of about 224 (that of *n*-hexadecene). The polystyrenes should have a molecular weight within a range of from about 10,000 to 75,000, preferably 30 to 60,000 Staudinger. These molecular weights correspond to intrinsic viscosities within the range of from 0.2 to 2.0, preferably 0.8 to 1.0. The alkylating agent contemplated contains 12 to 20 carbon atoms in a straight chain. A chlorinated aromatic hydrocarbon is used as a solvent and a Friedel-Crafts catalyst in amounts varying between about 10 and 20% by weight based on the weight of the polystyrene. The preferred catalyst modifier, nitrobenzene, is present in amounts so that the mol ratio of nitrobenzene to the catalyst is from 0.2 to 0.8. Reaction temperatures within a range of from 80° to 150° F. are used. These operable reaction conditions are so adjusted that in the relationship

$$K = \frac{CT}{(1+R)^2}$$

K varies between 6.0 and 15, where C equals the weight ratio of catalyst to polystyrene, T is the temperature ° F., and R is the ratio of mols of catalyst modifier to mols of aluminum chloride. By this particular process advantageous yields of an alkylated polystyrene pour depressant having an overall activity in a wide range of lubricating oils may be obtained.

As pointed out heretofore, the pour depressant agents have a cryoscopic molecular weight in the range from about 700 to 3,000 and an intrinsic viscosity in the range from about 0.1 to 0.5. These compounds are used in a weight concentration of about 0.002 to 0.20. A somewhat more preferred concentration is in the range from about 0.005 to 0.5 weight percent. A very desirable concentration to be used is in the range from about 0.01 to 0.3 weight percent.

The second class of pour depressants to be used in

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conjunction with the acylated polystyrene as described above are copolymers of ethylene and a vinyl acetate. It is preferred that the parts by weight of ethylene in the copolymer be in the range from about 60 to 99% as compared to parts by weight of vinyl acetate in the range from about 40 to about 1%. A very desirable ethylene-vinyl acetate copolymer contains from about 15 to 25% by weight of vinyl acetate, as for example about 20% parts by weight of vinyl acetate.

The molecular weights of the ethylene-vinyl acetate copolymer are critical and should be in the range from about 1,000 to 3,000, preferably in the range from about 1,500 to 2,200. The molecular weights are determined by K. Rast's method (Ber. 55, 1051, 3727 (1922)).

The ethylene-vinyl acetate copolymer as described above is used usually in a concentration in the range from about .001 to .5% by weight, preferably in a concentration in the range from about .005 to .1% by weight. The low molecular weight copolymers may be prepared by any peroxide process. In some instances, it may be desirable to first prepare a higher average molecular weight polymerization product and then recover from that product material having a molecular weight within the range between about 1,000 and about 3,000. Since such polymerization products normally consist of a smear of polymers whose molecular weights vary over a wide range, an effective method for recovering the 1,000 to 3,000 molecular weight portion therefrom is to extract the product with a solvent such as normal heptane or methyl-ethyl ketone. Other methods for obtaining the low molecular weight materials include thermal degradation of the high molecular weight polymer with ozone in order to break the polymer chains. Still other methods also useful will be apparent to those skilled in the art.

A very desirable method is to conduct polymerization in a benzene solution using di-tertiary-butyl-peroxide as an initiator at a temperature in the range from about 280° to 340° F. The preferred temperature is about 300° F. The pressure is in the range from about 700 to 2,000 pounds, preferably at about 800 pounds. The autoclave or similar equipment containing the solvent, initiator and vinyl acetate is purged about three times with nitrogen, twice with ethylene and then charged with a sufficient amount of ethylene to yield the desired pressure when heated to the reaction temperature. During the polymerization, additional ethylene is added whenever the pressure drops by about 100 p.s.i.g. Polymerization is considered complete when it is less than 50 p.s.i.g. pressure drop per hour. The product is stripped free of solid and unreacted vinyl acetate under vacuum.

Various amounts of the pour depressants and the various salts were utilized in distillate fuels. A typical distillate fuel boiling in the range from 250° to 750° F. to which the present additives may be added are middle distillate heating oils. These fuels are of commercial grade and have typical properties as follows:

Composition:	
Straight run gas oil	40
Cat. cracked gas oil	60
Inspections:	
Gravity, ° API	29.1
ASTM pour, ° F., no additive	+20
Flash Pensky-Martin, ° F.	192
Distillation ASTM, ° F.:	
I.B.P.	398
10%	492
50%	566
90%	612
F.B.P.	644

The improvements obtained by adding the additives in accordance with the present invention are set forth in the following table. All pour points quoted hereafter were obtained by ASTM Method D-97-47.

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The total amount of the pour depressant utilized is preferably in the range from about 0.001 to 0.500 weight percent based upon the amount of base stock. It is preferred that a total amount of pour depressant be in the range from about 0.002 to 0.100 weight percent. The relative amounts of the acylated polystyrene as compared to the alkylated polystyrene or the copolymer of ethylene and vinyl acetate may vary broadly as for example from 10 to 90 weight percent of the acylated polystyrene to 90 to 10 percent of either the alkylated polystyrene or the copolymer. However, it is preferred that the range be from about 25 to 75 weight percent of the acylated polystyrene as compared to 75 to 25 weight percent of either the alkylated polystyrene or the copolymer.

The synergistic effects secured by the particular mixture of compounds hereinafter described are illustrated by the data in the following Table I. It will be noted that replacement of half the more active pour depressant with the less active pour depressant does not give the expected reduction in activity. Instead, the mixture is usually more active than an equal concentration of either component. This can result in appreciable savings of polymer required to reach a given pour point, with a consequent reduction in cost.

TABLE I

Synergistic Combinations of Pour Depressants

Base stock description	Total wt. percent polymer	Pour Point, °F., With Additive Indicated		
		(A) Acyl polystyrene ¹	50/50 mixture (A)+(B)	(B) Component
I. (B) Component is Alkyl Polystyrene ² :				
Straight Run Heating.....	0.01	0	-5	-5
Oil from Canadian.....	0.02	-15	-20	-20
Crude, +15° F.....	0.03	-20	-30	-25
Original Pour Point ⁴				
II. (B) Component is Ethylene/Vinyl Acetate Copolymer ³ :				
Straight Run Heating.....	0.01	-10	-5	-5
Oil from Venezuela.....	0.02	-15	-20	-10
Crude, +10° F.....	0.03	-20	-30	-20
Original Pour Point ⁵	0.05	-25	-35	-25
Straight Run Heating.....	0.01	0	-5	+5
Oil from Canadian.....	0.05	-20	-25	-15
Crude, +15° F.....	0.10	-30	-35	-25
Original Pour Point ⁴				

¹ Product prepared by acylating polystyrene with 0.25 mole decanoyl chloride, 0.50 mole dodecanoyl chloride and 0.25 mole tetradecanoyl chloride per mole of phenyl groups. Intrinsic viscosity 0.055.

² Product prepared by alkylating polystyrene with 0.09 mole C₁₂, 0.18 mole C₁₄, 0.40 mole C₁₆, 0.27 mole C₁₈, and 0.06 mole C₂₀ n-olefins per mole of phenyl groups. Intrinsic viscosity 0.122, cryoscopic molecular weight 925.

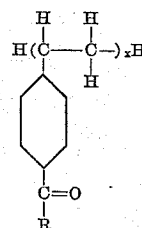
³ Product contains 84 wt. percent ethylene and 16 wt. percent vinyl acetate. Intrinsic viscosity 0.124, cryoscopic molecular weight 1150.

⁴ Boiling range 316-685° F., 39.0 API gravity, 3.25 cs. at 100° F. viscosity

⁵ Boiling range 354-624° F., 37.4 API gravity, 2.35 cs. at 100° F. viscosity

What is claimed is:

1. A petroleum distillate fuel composition having an improved pour which comprises essentially a petroleum distillate fuel boiling in the range from about 250° F. and about 750° F. which has been improved with respect to pour point by the incorporation therein of a pour depressing effective amount in the range from about .001% to .05% by weight of a blend consisting essentially of about 10% to 90% by weight of an acylated polystyrene having a structural formula as follows:



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wherein R is a straight chain alkyl group of about 7 to 15 carbon atoms and x is a number from 3 to 20 and 90% to 10% by weight of a compound selected from the class consisting of an alkylated polystyrene and a copolymer of ethylene and vinyl acetate, said copolymer being characterized by having a molecular weight in the range from about 1000 to 3000 and being further characterized by containing from about 1% to 40% by weight of vinyl acetate in the copolymer, said alkylated polystyrene being characterized by having a molecular weight in the range from about 700 to about 3000 and being further characterized by having one alkyl group containing from about 14 to about 18 carbon atoms per ring.

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2. The fuel composition of claim 1 wherein said blend consists essentially of 40 to 60% by weight of said acylated polystyrene and 60 to 40% by weight of a compound selected from the class consisting of an alkylated polystyrene, and a copolymer of ethylene and vinyl acetate.

3. The fuel composition of claim 1 wherein the molecular weight of the copolymer of ethylene and vinyl acetate is in the range from about 1500 to 2200.

References Cited in the file of this patent

UNITED STATES PATENTS

2,499,723	Coffman et al. -----	Mar. 7, 1950
2,703,817	Serniuk -----	Mar. 8, 1955