

1

3,529,944

PROCESS FOR CLARIFYING AND STABILIZING HYDROCARBON LIQUIDS

Arnold M. Leas, Ashland, Ky., assignor to Ashland Oil & Refining Company, Houston, Tex., a corporation of Kentucky

No Drawing. Continuation-in-part of application Ser. No. 276,865, Apr. 30, 1963. This application Jan. 23, 1967, Ser. No. 610,762

Int. Cl. C10I 1/18, 1/22

U.S. Cl. 44—70

6 Claims

ABSTRACT OF THE DISCLOSURE

A method for clarifying and stabilizing hydrocarbon liquids which are subject to oxidative deterioration, particularly jet fuels, which includes adding to the fuel a material which accelerates the oxidative deterioration of the fuel, such as a polyphenyl substituted lower alkane or lower alkylene, an alkanol ester of citric acid or acetoxy ethyl monobutylether; passing the hydrocarbon liquid through the solid, particulate, adsorbent media to remove microimpurities and the products of oxidative deterioration; and thereafter adding additional amounts of a stabilizing material to stabilize the hydrocarbon liquid against further oxidative deterioration.

The present application is a continuation-in-part of application Ser. No. 276,865, filed Apr. 30, 1963, and now abandoned.

The present invention relates to a novel process for refining and/or reclaiming hydrocarbon liquids, such as jet fuels, hydraulic fluids and lubricants and other crude oil derivatives. In a more specific aspect, the present invention relates to a process for refining and/or reclaiming hydrocarbon liquids, including jet fuels, hydraulic fluids and lubricants to improve their properties, particularly, their stability, clarity and lubricity.

It is a generally accepted fact that the production of jet fuels is a most demanding proposition and that any process capable of delivering a clean and stable jet fuel will likewise be capable of processing other hydrocarbon liquids to similarly clean and stabilize them. Accordingly, the present discussion will be confined primarily to the treatment of jet fuels with the understanding that the process of the present invention is equally applicable to the treatment of hydrocarbon liquids requiring similar treatments but having specifications which are less stringent.

Hypothetically the shortest distance between two points would be to connect the production nozzle of a refinery producing jet fuel to the inlet of the combustion nozzle within a jet engine. However, this is obviously physically impossible and to approach it is highly impractical. It must be recognized that refiners or producers of fuel need to blend, store, test, and schedule loading and transportation to meet needs of a customer, who, in turn, will need to store a sufficient quantity for normal usage and unexpected contingencies. In most instances, the fuel in question will have had an opportunity to accumulate normal contaminants during storage and transit. This normal incipient degradation period during storage and

2

transit, strangely enough, provides a useful and natural time for the most deleterious, dynamic physical, chemical and biological kinetic reactions to complete their offensive deterioration of the fuel. In addition, it must be recognized that fuels can vary considerably when originating from many different crude oil sources, refinery processes, shipping and storage containers, fuel handling procedures, testing procedures and additive treatments.

When it has heretofore been proposed that the by-products of storage and/or transportation or other contaminants be removed from the fuel at the use point loading tank farm, no adequate system for this purpose has been provided. Conventionally, a plurality of what are known as "filter coalescers" are used in series at the aircraft loading tank farm. However, these filter coalescers have failed to properly process supersonic jet fuels inasmuch as such fuels must now be essentially free of soluble chemical and biological contaminants, as well as insoluble sediment, when delivered to the aircraft.

More expensive alternatives to the use of the filter coalescer, or, in addition to the filter coalescer, which have been proposed, include, over-refining at the production point, redesigning aircraft engines, discarding residual fuel from returning aircraft, flushing the aircraft with clean fuel and discarding the same, speeding the fuel from the refinery in clinically clean facilities and maintaining minimal contact with oxygen during transport. Other equally unattainable or expensive approaches are specifying rigid thermal stability tests for delivered fuel; providing additional new all-purpose additives which will overcome all of the problems of production transportation, storage and loading; discovering new and better techniques and equipment that will drastically improve jet fuel production, transportation, storage, filtering and loading; or redistilling degraded fuel at the point of use.

A clean jet fuel is defined by the industry as a fuel which contains less than 2.0 milligrams of solids per gallon, retained on a 0.45 micron filter paper. A thermally stable jet fuel is defined as a fuel which leaves no visible varnish deposits on heat exchanger metal surfaces and does not form solid particles, tending to plug jet engine fuel filters or fuel inspection nozzles.

It is well known to those familiar with this art that thermal stability for jet fuels is the most difficult quality to obtain and maintain in practice, yet it is the most important property of the fuel to control.

Jet engines, and particularly the engines of supersonic and hypersonic jet aircraft, are operated at extremely high temperatures. In such use, the fuel is often used as a heat sink for the aircraft via the heat exchangers and injection nozzles in the engine. The fuel may also be subjected to elevated temperatures, during storage in wing tanks on supersonic aircraft, resulting from the absorption of heat from the surface of the wing. In some cases, the fuel may be subjected to elevated temperatures, for several hours prior to combustion, in the range of 400 to 700° F. for supersonic aircraft and to considerably higher temperatures up to the point of initiation of endothermic reactions for hypersonic aircraft. Many, if indeed not all, jet fuels tend to be relatively unstable when subjected to high temperatures below the combustion point, thus tending to form heavy solid or semi-solid par-

ticles which, in turn, cause heat exchanger fouling, jet nozzle plugging and other undesirable effects. Fuel thermal instability not only reduces the operational life of the engine but may present a hazard to flight operation. Accordingly, a very serious need to improve the thermal stability of a wide range of jet fuels has arisen.

The thermal stability of jet fuels is measured in the industry by the so called ASTM-CRC standard, modified CRC, and research CRC coker tests. In these tests, the fuel is subjected to conditions generally simulating the adverse conditions to which it is subjected in actual use. In the research coker test, for example, the fuel is heated in a reservoir to a temperature corresponding to the temperature of fuel in the aircraft wing tanks. (In the standard coker test, a heated reservoir is not used, thus, this arrangement corresponds to aircraft when the fuel is essentially at ambient temperatures in the tanks.) From the reservoir the fuel is pumped through a preheater tube at a higher temperature, corresponding to the temperature of the heat exchanger in the jet engine, and on through a filter at a still higher temperature, corresponding to the temperature at the entrance to the combustion nozzle. This filter removes non-liquid particles which have been formed at the elevated temperatures. The hot filter simulates the conditions to which the fuel is subjected as it passes through the fuel injection nozzles in the engine immediately prior to combustion. The operating conditions of the test can be varied to correspond to various use conditions. Coker test conditions are usually expressed in abbreviated form; for example 200-400/500/6, meaning that the reservoir temperature is 200° F., the preheater temperature 400° F., the filter temperature 500° F., and the fuel flow rate 6 pounds per hour.

At the present time, the fuels to be used in Mach 3 plus jet aircraft utilize coker conditions of 300-500/600/6, and, in the future, it is expected that these conditions will be further increased in severity to 300-600/700/6.

The results of the coker tests are expressed in terms of a rating code, indicating, relatively, the quantity of varnish deposit left in the preheater, ranging from 0, for the best, to 8, for the worst, and in terms of the pressure drop in inches of mercury across the filter, ranging from 0, for the best, to 25 inches, for the worst. The high thermal stability demanded of Mach 3 plus jet fuels is indicated by the fact that they must have a preheater code rating less than 3 and a filter pressure drop of less than 5 inches of mercury.

Considerable difficulty has been experienced in delivering, at the point and time of use, fuels which will meet and pass the coker test specifications outlined. Even though the fuel may have passed these coker tests at the refinery, transportation from the refinery to the point of use or standing in storage for a period of time frequently degrades a fuel to a point that it can no longer pass these tests. Such degradation is caused by a whole host of factors, but in the end the underlying causes of such degradation appear to be extremely complex and are not fully understood by those skilled in the art. It is believed that at least a part of the problem results from both solid and dissolved microimpurities which may exist in, enter or be formed in the fuel during storage and transit. Most bulk containers, storage facilities and pipe lines used for fuel transportation are being constructed of mild steel. Accordingly, they are subject to flaking-off of metal oxides into the fuel during intermittent filling and unloading. This condition can be minimized by the use of special linings but such linings in themselves introduce some impurities, and even with aluminum, stainless steel, or lined carbon steel shipping and storage containers, large quantities of jet fuel have become degraded with respect to thermal stability and are found unsuitable for use at the terminal. Other impurities such as silica-alumina, sulfur, nitrogen, oxygen, halogens, water, bacteria, fungi, gums, peroxides, organic particles, catalysts residues, other treating residues

and surfactants may also be present individually or in combinations. These microimpurities are usually not even apparent to the naked eye, yet the normal processing and handling of a fuel may permit sufficient accumulation of such impurities to initiate and propagate dynamic forces which work to degrade the thermal stability of the fuel later on. The effect may be catalytic, in which impurities promote reactions producing thermally unstable compounds in the fuel. Additives themselves, which are incorporated in the fuel to improve its properties, are believed to be degraded under some conditions and, in some instances, to cause degradation. In any event, a good part of the difficulty of overcoming degradation of fuels has resulted from the fact that the causes are multitudinous and there are very few which have been isolated and actually proven to be responsible for degradation.

It is therefore an object of the present invention to provide a novel process which solves substantially all of the above-mentioned problems. Another object of the present invention is to provide a novel process for refining and/or reclaiming liquid hydrocarbons, particularly jet fuels, hydraulic fluids and lubricants. Still another object of the present invention is to provide a novel process for refining and/or reclaiming liquid hydrocarbons, including jet fuels, hydraulic fluids, and lubricants which is suitable for use either at the point of production or at the point of use. A still further object of the present invention is to provide a novel process for converting a good hydrocarbon liquid, particularly an aircraft fuel, into a better quality product. A still further object of the present invention is to provide a novel process for converting a storage-degraded hydrocarbon liquid into a high quality product. Another and further object of the present invention is to provide a novel process for the removal of sub-micronic particle matter and soluble chemical and biological contaminants from degraded hydrocarbon liquids. Yet another object of the present invention is to provide a novel process for rehabilitating unused hydrocarbon liquids, particularly aircraft fuels, from use vehicles. Another and further object of the present invention is to provide an improved process for treating hydrocarbon liquids which eliminates the necessity of nearly all additives during production, transportation and storage of hydrocarbon liquids, but which permits minimum injection of additives at the point of use and particularly at a jet fuel loading facility. A still further object of the present invention is to provide a novel process for the treatment of hydrocarbon liquids which will permit the continued use of clean, carbon steel containers and/or lined containers in the transportation and storage of hydrocarbon liquids, particularly aircraft fuels. Another and further object of the present invention is to provide an improved process for the treatment of hydrocarbon liquids, particularly aircraft fuels, which will permit the use of hydrocarbon products from a wide variety of crude oil sources; which have been subjected to a wide variety of refining processes; which have been shipped and stored in a large number of different containers; and which have been subjected to a large number of different handling procedures, test procedures and additive treatments. A further object of the present invention is to provide an improved process for treating aircraft fuels which will result in a minimum rejection of degraded fuels and make possible maximum in-flight safety with minimum tankage and inventory at the point of use. A still further object of the present invention is to provide an improved process for the treatment of hydrocarbon liquids, particularly aircraft fuels, hydraulic fluids, and lubricants in an economic manner yet which produces a clean, thermally stable product. These and other objects and advantages of the present invention will be apparent from the following detailed description.

In accordance with the present invention, microimpurities are removed from hydrocarbon liquids by passing the liquid through a solid, particulate adsorbent media.

In accordance with a further aspect of the present invention, this selective adsorption of the hydrocarbon liquid is further improved by the addition of promoting agents to the liquid prior to filtration and/or the addition of additives to the hydrocarbon liquid after filtration.

Specific reference will be made hereinafter to the treatment of jet fuels since these materials require more complex treatments and must meet the most demanding specifications of any hydrocarbon liquid products. It has thus been found that the passage of jet fuels through the adsorbent media of the present invention is highly effective in removing dissolved impurities as well as spent additives, free peroxides, metal chelates, metallo-organic compounds, free metal particles, dirt, bacteria, fungi and other microimpurities. The novel process of the present invention has been found to be particularly useful in the treatment of jet fuels after normal degradation in transportation or storage or after promoted or catalyzed degradation by the addition of the aforementioned promoting agents prior to treatment with the adsorbent media.

Suitable adsorbent materials for use in accordance with the present invention include various types of natural or synthetic clays, either treated or untreated, fuller's earth, attapulgite, silica gel, and adsorbent catalysts.

The adsorbent solid filter material is preferably graded to 30 to 60 mesh. After passage through this fine clay, the hydrocarbon liquid is preferably passed through a similar adsorbent body of solid, particulate adsorbent material of a slightly larger particle size, for example, clay of 8 to 15 mesh.

While the subject particle-form, adsorbent material is highly effective in the removal of microimpurities from hydrocarbon liquids, the fineness of the adsorbent material sometimes results in entrainment of particles of adsorbent in the treated liquid. Accordingly, it is preferable to pass the hydrocarbon liquid which has been treated with adsorbent solid through a bed of solid, inert particle-form material. More specifically, fine metallurgical slag followed by coarse metallurgical slag may be used as an inert medium following the adsorbent treatment. Other inert media such as glass beads, or the like, may be used, or a heavy mat of glass wool or plastic membranes can be used to prevent the fine adsorbent material from being carried out with the treated hydrocarbon liquid.

The effectiveness of the present filtration technique is illustrated by the series of tests outlined below. In these tests, a variety of fuels, having reasonably low water contents, were filtered through the fine, followed by the coarse, adsorptive clay and thence through the coarse, followed by the still more coarse, metallurgical slag, previously referred to. Research Coker tests were performed at 300-500/600/6, in runs No. 1 through 4. In run No. 3, the fuel was a supersonic jet fuel which has been prestressed by heating for 48 hour at 300° F. This artificial thermal stressing simulates the situation where a fuel has been subjected to prolonged heating and storage in the wing tanks of a jet aircraft but which has not been actually utilized in the aircraft. In run No. 4, a less exotic jet fuel was tested under Standard Coker test conditions of 425/525/6. In this series of tests, a peroxide number was obtained in some cases. The peroxide number is a measure of the number of gram equivalents of active oxygen per 1,000 liters of gasoline. This is an important indicator in the hydrocarbon fuel field since peroxides are formed by the oxidation of unsaturated hydrocarbons and it is believed that such peroxides are intermediates or precursors in the formation of gums and other polymer materials prior to and during actual use of the fuel. The peroxide number is obtained by reacting a sample of the gasoline with ferrous sulfate, in a water-acetone solution, and, thereafter, determining the ferric sulfate formed by titration with titanous chloride. From the quantity of

ferric sulfate formed, the peroxide number is calculated. Table I below summarizes the results of these tests.

TABLE I

Material	Preheater code No.	Filter pressure differential, inches Hg.	Dirt content, mg./gal.	Peroxide No., mg./1,000 gal.
Untreated supersonic jet fuel from tank car---	6	2.5	18	-----
(1) Treated supersonic jet fuel from tank car---	2	0.1	0.4	-----
Untreated supersonic jet fuel from tank car---	7	25	24	-----
(2) Treated supersonic jet fuel from tank car---	0	0	0.9	-----
Untreated prestressed supersonic jet fuel-----	8	25	33	96
(3) Treated prestressed supersonic jet fuel-----	2	1.2	2.1	1.1
Untreated JP-6 jet fuel-----	3	12.9	2.4	2.4
(4) Treated JP-6 jet fuel-----	1	0.0	0	0

While, as indicated by the previous examples, the filtering technique of the present invention is highly effective in the removal of microimpurities, particularly from fuels which have been transported or stored and thereby degraded over a substantial period of time, the effectiveness of the filtration process can be greatly improved and the life of the filter substantially prolonged if certain promoting agents which apparently promote oxidation and speed up certain types of degradation are added to the hydrocarbon liquid prior to filtration. Generally, such pretreatment or the addition of promoters should take place at the production point so that the fuel or other hydrocarbon liquid will be both naturally degraded and degraded by virtue of the promoting or catalytic characteristics of the promoters prior to passage through the adsorptive media. Specifically, it has been found in accordance with the present invention that certain known antioxidants and metal deactivators as well as a group of new promoters have a peculiar affect on the filtration process of the present invention. It has been found that if such promoting agents and/or additives are added to the fuel prior to filtration, the filtered fuel is substantially superior in its thermal stability to a fuel which has not received the promoting agents prior to being filtered.

One particular promoter which has been found highly effective in conjunction with the adsorbent filtration of the present invention and is believed to act as a promoter for artificial oxidation and/or degradation of hydrocarbon liquids is a group of polyphenyl substituted lower alkanes and lower alkenes. These phenyl compounds also have been found to have unexplainable antioxidant or stabilizing effects even though the adsorbent appears to remove most of the promoter. When these promoters, either alone or in combination with other materials, are added to a fuel, they have a tendency to prevent the formation of some oxygenated products in the fuel, during transportation and/or storage; and also, apparently, form or promote the formation of other oxygenated compounds thereby removing precursors of subsequent oxidation from the fuel. Thereafter, when a fuel treated with these compounds is filtered through the adsorbent material of the present invention, the oxygenated compounds formed by natural or promoted degradation are completely removed from the fuel. Preferably, these promoters are added to the fuel at the production point, so that they are present during any subsequent storage and/or transport, and the fuel is filtered through the adsorbent filter of the present invention just prior to use, such as the loading of the tanks of the jet aircraft. It has been found that 0.0001 to 0.1% by weight of these phenyl compounds, when added to the hydrocarbon liquid, will produce good results. Phenyl compounds falling within the present invention include diphenylmethane; triphenyl-

methane; 1,2-diphenylethylene; 1,1,2,2-tetraphenylethylene; 1,1,2-triphenylethane; and 1,1,2,2-tetraphenylethane. The following table illustrates the benefits of first treating a fuel with phenyl promoting agents and thereafter filtering the fuel through the adsorbent filter of this invention.

TABLE II.—SST-JP-5 TYPE JET FUELS WITH VARIOUS TREATMENTS OF PHENYL TYPE PROMOTING AGENTS FOLLOWED BY ADSORBENT TYPE FILTRATION

	Coker 350/450/6		Dirt content, mg./gal.
	Preheater, code No.	Filter, in. Hg	
(1) Original fuel with no filtration....	6	25	7.8
(2) Original fuel with filtration.....	4	18	2.9
(3) Original fuel plus 0.001% di-phenylmethane then filtered.....	2	0.9	1.7
(4) Original fuel plus 0.001% tri-phenylmethane then filtered.....	1	1.1	2.2
(5) Original fuel plus 0.001% 1,2-di-phenylethylene then filtered.....	3	2.6	3.7
(6) Original fuel plus 0.001% 1,1,2,2-tetraphenylethylene then filtered....	1	1.4	2.6
(7) Original fuel plus 0.001% 1,1,2-triphenylethane then filtered.....	2	2.3	1.6
(8) Original fuel plus 0.001% 1,1,2,2-tetraphenylethane then filtered.....	1	1.6	2.2

NOTE: Filtration through three feet of attapulgit clay.

Another additive, which has been found particularly useful as a promoter for promoting artificial degradation of hydrocarbon liquids, particularly jet fuels, is acetoxyethylmonobutylether, and this material in combination with other promoting agents and/or conventional jet fuel additives. This particular material has a major affect upon the high temperature stability of hydrocarbon liquids, and, particularly jet fuels. However, it also has an unexpected affect when utilized as a promoter prior to adsorptive filtration of hydrocarbon liquids. The acetoxyethylmonobutylether may be added to the hydrocarbon liquid fuel at the production point or at the use point prior to filtration.

The following table illustrates the effectiveness of the ether compound followed by filtration through adsorbent clay.

TABLE III.—JP-6 TYPE JET FUELS WITH VARIOUS TREATMENTS OF ETHER (ACETOXYETHYLMONOBUTYLETHYL) TYPE PROMOTING AGENTS FOLLOWED BY ADSORBENT TYPE FILTRATION

	Coker 450/550/6		Dirt content, mg./gal.
	Preheater, code No.	Filter, in. Hg	
(1) Original fuel with no filtration....	6	25	6.6
(2) Original fuel with filtration.....	5	12.7	2.4
(3) Original fuel plus 30 pounds BCA/1,000 bbls. then filtered.....	3	2.1	1.7
(4) Same as item 3 then inject 30 BCA/1,000 barrels.....	2	1.4	1.8
(5) Original fuel plus 60 pounds BCA/1,000 barrels then filtered.....	2	0.8	1.5
(6) Same as item 5 then inject 60 pounds BCA/1,000 barrels.....	1	0.9	0.9
(7) Original fuel plus 60 pounds BCA and 3 pounds MD/1,000 barrels then filtered.....	0	0.6	1.3
(8) Original fuel plus 3 pounds MD/1,000 barrels then filtered.....	4	15.4	2.2

NOTE:

- (1) BCA expressed as acetoxyethylmonobutylether.
- (2) MD expressed as conventional metal deactivator.
- (3) Filtration through three feet of attapulgit (30/60 mesh) clay.

Still another group of materials found to be effective promoters, for degradation of hydrocarbon liquids, are low molecular weight esters of citric acid. Examples of these esters include acetoxytributyl citrate, tributyl citrate, acetoxytri-2-ethylhexyl citrate, etc. These additives can also be added to the fuel at the production point or the use point prior to adsorptive filtration, in amounts of about 0.001 to 2.0% by weight, and may be used in combination with other promoters and/or conventional jet fuel additives.

The following example illustrates the effectiveness of the above-mentioned esters in conjunction with adsorptive filtration.

TABLE IV.—JP-6 TYPE JET FUELS WITH VARIOUS TREATMENTS OF CITRIC ACID ESTERS AS PROMOTING AGENTS FOLLOWED BY ADSORBENT TYPE FILTRATION

	Coker 500/600/6	
	Preheater, code No.	Filter, in. Hg
10 (1) Original fuel with no filtration.....	7	25
(2) Original fuel with filtration.....	6	25
(3) Original fuel plus 30 pounds TBC/1,000 barrels then filtered.....	4	5.2
(4) Same as item 3 then inject 30 pounds TBC/1,000 barrels.....	3	4.9
(5) Original fuel plus 30 pounds, TBC and 1 MD/1,000 barrels then filtered.....	3	1.7
15 (6) Original fuel plus 30 pounds TBC and 2 pounds MD/1,000 barrels plus 30 pounds BCA per 1,000 barrels fuel then filtered.....	6	0.9
(7) Same as item 6 then inject 30 pounds BCA plus 2 pounds MD per 1,000 barrels fuel.....	1	0.4

NOTE:

- (1) TBC expressed as tributylcitrate.
- (2) MD expressed as conventional metal deactivator.
- (3) Filtration through three feet of attapulgit (30/60 mesh) clay.

It has also been found that in addition to the removal of oxygenated compounds, other impurities and precursors of gums and the like from hydrocarbon liquids, the adsorptive filter media also removes all or a substantial part of the promoters of the present invention as well as other conventional hydrocarbon liquid additives. Accordingly, the preferred technique in accordance with the present invention is to add only a minimal amount of these promoting agents to the hydrocarbon liquid at the production point immediately after production and before any storage and/or transportation and thereafter, add an additional amount of the promoter as a stabilizing agent and all or a majority of conventional additives after filtration through the adsorptive media. For example, about 0.001 to 2% by volume of these promoters can be added to the hydrocarbon liquid at the production point prior to any substantial storage and/or transportation delay. The fuel or other hydrocarbon liquid is then transported to the use point and stored and is thereafter filtered through the adsorptive filter just prior to use. Following filtration through the adsorptive filter, and prior to loading of the use vehicle, such as a jet aircraft, an additional 0.1 to 2% by volume of the additive is incorporated in the fuel to improve the stability of the fuel. This same procedure should preferably be followed where conventional antioxidants, metal deactivators and other additives are incorporated in the fuel at the production point and prior to adsorptive filtration.

It has also been discovered in accordance with the present invention that the previously mentioned promoting agents are quite effective when combined with known antioxidants and metal deactivators heretofore used as additives for jet fuels and the like.

One particularly effective additive which, when combined with the previously mentioned promoters, is highly effective in the promotion of artificial degradation of fuels is a material commercially available as a metal deactivator (50 to 100% active ingredient), specifically, N,N'-disalicylidene-1,2-propanediamine or its homolog N,N'-disalicylidene-1,2-ethanediamine. When combined with one of the previously mentioned promoting agents, the proportions should be about 85 to 99% of promoting agent plus 15 to 1% of the diamine. The blend is then utilized in the same amounts previously set forth for the promoters.

Another known additive, heretofore considered an antioxidant for jet fuels is 2,6-ditertiary-butyl-paracresol. This material may also be combined with the previously mentioned promoters in the amounts set forth above to produce a synergistic affect in the promotion of artificial degradation and subsequent stabilization of hydrocarbon liquids, when these materials are added to the liquid prior to adsorptive filtration.

Another group of conventional additives, which have previously been added to some jet fuels as suspending agents or dispersants, is a mixed polyamine product known as "jet fuel additive 5" "JFA-5." The combination of this material with the promoters set forth above should be approximately the same as previously mentioned for the other blends and may be added to the fuel in the amount previously mentioned prior to adsorptive filtration.

The following examples illustrate the effectiveness of the blends of promoting agent plus additive prior to adsorptive filtration as well as such additions before and after filtration. AO refers to an anti-oxidant, namely 2,6-ditertiary butyl paracresol; ATBC refers to acetyl tributyl citrate; and TEHC refers to tri-2 ethylhexyl citrate.

N,N'-disalicylidene-1,2-alkyldiamine, and mixtures of at least one of said promoting agents with other additives; consisting of metal deactivators, antioxidants and dispersants; and thereafter passing said hydrocarbon fuel through a solid, particulate, adsorbent media to remove microimpurities and the products of said oxidative deterioration therefrom.

2. A method in accordance with claim 1 wherein the promoting agent is added in an amount of about 0.0001 to 2% by weight of the total hydrocarbon liquid.

3. A method in accordance with claim 1 wherein a stabilizing agent is added to the hydrocarbon liquid after passage of said hydrocarbon liquid through the adsorptive media, said stabilizing agent being selected from the group

TABLE V

Run No. and fuel	Additives, lbs./1,000 bbls. of fuel							Coker test conditions	Preheater code No.	Filter P, in. Hg	Dirt content, mg./gal.
	AO	BCA	MD	JFA-5	TBC	ATBC	TEHC				
Mach 3								300-500/600/6	3	19.1	
(1) Mach 3		50						300-500/600/6	2	0.1	
Mach 3								300-500/600/6	4	1.2	
(2) Mach 3		50						300-500/600/6	0	0.4	
Mach 3	8							300-600/700/6	7	12.5	
(3) Mach 3	8	60						300-600/700/6	4	4.4	
(4) Mach 3	8	50						300-600/700/6	5	6.3	
(5) Mach 3	8		2					300-600/700/6	6	10.2	
Mach 3								300-500/600/6	3	0.1	0.4
(6) Mach 3		(1)	(2)					300-500/600/6	1	0	0
Mach 3								300-500/600/6	7	25	24
(7) Mach 3		(1)	(2)					300-500/600/6	3	0.2	0.7
JP-6								425/525/6	3	12.9	
(8) Mach 3		(1)	(2)					425/525/6	1	0.0	
Kerosene								175-450/550/6	6	0.65	
(9) Mach 3		(3)	(4)					175-450/550/6	2	0.1	
Kerosene								300-500/600/6	7	21.4	
(10) Mach 3		(5)	(6)					300-500/600/6	2	1.8	
Paraffinic jet fuel								300-550/650/6	4	2.6	
(11) Paraffinic jet fuel		(7)	(8)					300-550/650/6	2	0.0	
Mach 3	8							300-600/700/6	7	12.5	
(12) Mach 3	8	58	2					300-600/700/6	2	2.6	
(13) Mach 3	8	48	2					300-600/700/6	4	2.1	
(14) Mach 3	8	48	2					300-600/700/6	3	4.1	
(15) Mach 3	8			10				300-600/700/6	7	0.5	
(16) Mach 3	8	40		10				300-600/700/6	2	0.3	
(17) Mach 3	8				20			300-600/700/6	4	5.7	
(18) Mach 3	8	30			20			300-600/700/6	1	0.8	
Mach 3								300-500/600/6	7	3.9	
(19) Mach 3		30			20			300-500/600/6	2	0.1	
Mach 3								300-500/600/6	5	20.2	
(20) Mach 3		60			40			300-500/600/6	1	0.0	
Paraffinic jet fuel								300-500/600/6	5	2.5	
(21) Paraffinic jet fuel		50			50			300-500/600/6	1	0.1	
Mach 3	8							300-600/700/6	7	12.5	
(22) Mach 3	8		2		20			300-600/700/6	2	1.8	
(23) Mach 3	8	30			20			300-600/700/6	1	0.8	
(24) Mach 3	8					20		300-600/700/6	4	8.4	
(25) Mach 3	8	30				20		300-600/700/6	2	2.1	
(26) Mach 3	8						20	300-600/700/6	4	10.5	
(27) Mach 3	8	30					20	300-600/700/6	1	2.2	
(28) Mach 3	8		2	10				300-600/700/6	5	0.4	
(29) Mach 3	8		2	10				300-600/700/6	5	0.5	
(30) Mach 3	8	38	2	10				300-600/700/6	1	0.0	
(31) Mach 3	8	38	2	10				300-600/700/6	2	0.1	
(32) Mach 3	8	28	2		20			300-600/700/6	0	0.6	
(33) Mach 3	8		2	10	20			300-600/700/6	2	0.4	
Paraffinic jet fuel								300-600/700/6	5	0.3	
(34) Paraffinic jet fuel		28	2		20			300-600/700/6	1	0.0	
(35) Paraffinic jet fuel	(9)	28	2		20			300-600/700/6	2	0.0	
Mach 3	8							300-600/700/6	7	12.5	
(36) Mach 3	8	28	2	10	10			300-600/700/6	0	0	
Mach 3								300-500/600/6	5	18	21
(37) Before filter		(10)	(11)					000-500/600/6	0	0	0
After filter			(11)		(10)			000-500/600/6	3	2.5	
Mach 3											
(38) Before filter		(10)	(11)		(10)			000-500/600/6	2	0.1	0
After filter			(11)		(10)			000-500/600/6	8	25	33
Prestressed Mach 3									4	5.7	
(39) Before filter		(12)	(13)		(12)			000-500/600/6	2	1.2	2.1
After filter			(13)								

¹ 96 vol. percent of 100. ² 4 vol. percent of 100. ³ 99 vol. percent of 100. ⁴ 1 vol. percent of 100. ⁵ 85 vol. percent of 100. ⁶ 15 vol. percent of 100. ⁷ 92 vol. percent of 60. ⁸ 8 vol. percent of 60.

⁹ 0.12% deicer. ¹⁰ 96 vol. percent of 00. ¹¹ 4 vol. percent of 30. ¹² 96 vol. percent of 50. ¹³ 4 vol. percent of 50.

What is claimed is:

1. A method for clarifying and stabilizing hydrocarbon liquids subject to oxidative deterioration; comprising, adding to a major proportion of said hydrocarbon liquid a minor proportion of a promoting agent, for accelerating the oxidative deterioration of said liquid selected from the group consisting of a phenyl compound selected from the group consisting of polyphenyl substituted lower alkanes and alkenes, acetoxy ethyl monobutylether, an oil-soluble, alkanol ester of citric acid, a mixture of acetoxy ethyl monobutylether and N,N'-disalicylidene-1,2-alkyldiamine, a mixture of an oil-soluble, alkanol ester of citric acid and

consisting of a phenyl compound selected from the group consisting of polyphenyl substituted lower alkanes and alkenes, acetoxy ethyl monobutylether, an oil-soluble, alkanol ester of citric acid, a mixture of acetoxy ethyl monobutylether and N,N'-disalicylidene-1,2-alkyldiamine, a mixture of an oil-soluble alkanol ester of citric acid and N,N'-disalicylidene-1,2-alkyldiamine, and mixtures of at least one of said promoting agents with other additives consisting of metal deactivators, antioxidants and dispersants.

4. A method in accordance with claim 3 wherein the stabilizing agent is added in an amount of about 0.0001 to

11

2% by weight of the total hydrocarbon liquid.

5. A method for clarifying and stabilizing a hydrocarbon liquid; comprising, passing said hydrocarbon liquid through a solid, particulate, adsorbent media and thereafter adding to said hydrocarbon liquid a minor proportion of a stabilizing agent selected from the group consisting of a phenyl compound selected from the group consisting of polyphenyl substituted lower alkanes and alkyl-
 enes, actoxy ethyl monobutylether, an oil-soluble alkanol ester of citric acid, a mixture of acetoxo ethyl monobutyl-
 ether and an N,N'-disalicylidene-1,2-alkyldiamine, a mixture of an oil-soluble, alkanol ester of citric acid and an N,N'-disalicylidene-1,2-alkyldiamine, and mixture of at least one of said stabilizing agents with other additives consisting of metal deactivators, antioxidants and disper-
 sants.

6. A method in accordance with claim 5 wherein the stabilizing agent is added in an amount of about 0.0001 to 2% by weight of the total hydrocarbon liquid.

12

References Cited

UNITED STATES PATENTS

2,343,430	3/1944	Wells et al.	210-59 XR
1,636,938	7/1927	Kauffman et al.	208-307
1,638,057	8/1927	Oberle	208-251
2,205,331	6/1940	Alton	208-306 XR

OTHER REFERENCES

A. W. Nash et al., The Principles of Motor Fuel Preparation & Application, N.Y., John Wiley & Sons, 1935, pp. 172-173.

DANIEL E. WYMAN, Primary Examiner

W. J. SHINE, Assistant Examiner

U.S. Cl. X.R.

44-73, 77, 80; 252-52, 79