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ADDITIVES FOR MODIFYING THE ELECTRICAL PROPERTIES OF COMBUSTIBLE ORGANIC LIQUIDS

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The present invention relates to additives for improving the properties of combustible organic liquids and more particularly relates to gasolines, aviation turbo-jet fuels, kerosines, solvents, and similar combustible liquids boiling in the range between about 75° F. and about 750° F. which have been improved with respect to their electrical properties by the incorporation therein of small amounts of quaternary ammonium salts of alkylenediamine polycarboxylic acids.

Studies have shown that large electrical charges are frequently built up during the handling and transportation of organic liquids boiling in the range between about 75° F. and about 750° F. and that the charges thus produced may be stored in the liquids until sufficient energy has accumulated for an electrical discharge to take place. When such charges are built up in gasolines, aviation turbo-jet fuels, kerosines, dry cleaning solvents and similar combustible liquids, the electrical discharge which results may ignite vapors in the air space above the liquid and produce an explosion. There is much evidence that many of the explosions which have occurred during the handling of such liquids during recent years can be attributed to such electrical discharges. Aviation turbo-jet fuels and certain solvents, carbon disulfide for example, have proved particularly hazardous insofar as such explosions are concerned because their vapors form explosive mixtures with air over relatively wide temperature ranges.

Although the exact mechanisms involved in the generation, accumulation and discharge of electrical energy during the handling of combustible liquids are not fully understood, it is known that the electrical conductivity of the liquids plays an important role. Increasing the conductivity of a liquid increases the rate at which charges are naturally dissipated and therefore charges sufficient to cause an explosion are less likely to accumulate. In general, it has been found that liquids having specific conductivities in the range of about 1×10^{-15} to about 1×10^{-12} mhos per centimeter are particularly hazardous and that the danger in handling such liquids can be materially reduced by increasing their conductivities to values greater than about 1×10^{-12} mhos per centimeter.

It has been suggested heretofore that various compounds be added to liquid hydrocarbons and similar combustible materials in order to increase their specific conductivity and thus reduce the danger of an explosion due to the generation, accumulation and discharge of electrical energy. Certain metallic compounds, particularly soaps of polyvalent metals and combinations of such soaps with other materials, have been said to be particularly effective. In practice, however, such additives have been found to be of little value because they are readily extracted by small quantities of water with which the liquids come into contact and because they adversely affect properties other than conductivity.

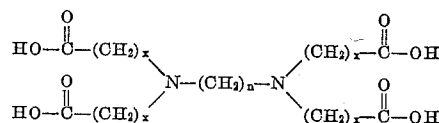
The present invention provides an improved class of additive materials for use in combustible organic liquids boiling in the range between about 75° F. and about 750° F. which greatly improve the electrical properties of such liquids and yet are free of undesirable charac-

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teristics which have prevented the widespread use of additives suggested for this purpose in the past.

In accordance with the invention, it has now been found that quaternary ammonium salts of alkylenediamine polycarboxylic acids can be employed to markedly increase the electrical conductivity of hydrocarbon oils and similar combustible organic liquids without adversely affecting the water tolerance, thermal stability, storage stability and other properties of the liquids. The additives are particularly effective for use in aviation turbo-jet fuels because they are ashless and hence, unlike most of the additives found effective for increasing conductivity heretofore, do not form deposits in the combustors and nozzles of turbo-jet engines. The additives of the invention thus have many advantages over additive materials taught by the prior art.

The additive agents employed to improve the electrical properties of combustible organic liquids in accordance with the invention are quaternary ammonium salts of alkylenediamine tetracarboxylic acids having from 2 to 4 carbon atoms in the alkylenediamine portion of the molecule and from 2 to 4 carbon atoms in each of the carboxylic acid substituent groups. Acids suitable for preparing such salts have the general formula



where x is an integer from 1 to 3 inclusive and n is an integer from 2 to 4 inclusive. Specific examples of such acids include ethylenediamine tetraacetic acid, ethylenediamine tetrapropanoic acid, ethylenediamine tetrabutanoic acid, propylenediamine tetraacetic acid, propylenediamine tetrapropanoic acid, propylenediamine tetrabutanoic acid, butylenediamine tetraacetic acid, butylenediamine tetrapropanoic acid and butylenediamine tetrabutanoic acid. Ethylenediamine tetraacetic acid is a preferred acid for preparing the additive agents of the invention because of its relatively low cost and ready availability.

The quaternary ammonium salts of alkylenediamine tetracarboxylic acids employed in accordance with the invention may be readily prepared by reacting an acid of the class described in the preceding paragraph with a quaternary ammonium hydroxide and thereafter removing the resulting water by means of an azeotropic distillation. The reaction is preferably carried out in the presence of a suitable solvent such as benzene, toluene or hexane. The ratio of acid to quaternary ammonium hydroxide employed may be varied widely and, depending upon the particular ratio used, the salt formed may have the particular ratio used, the salt formed may have from 1 to 4 quaternary ammonium groups. In general, the salts containing from 1 to 3 quaternary ammonium groups are somewhat more effective than the fully substituted salts. The use of mono quaternary ammonium salts is particularly preferred.

The quaternary ammonium hydroxides which are employed in preparing the salts of alkylenediamine tetracarboxylic acids as described above are those having substituent groups of from 1 to about 24 carbon atoms. The substituent groups may be alkyl, alkenyl, aromatic or cycloaliphatic groups. Examples of suitable quaternary ammonium hydroxides include tetramethyl ammonium hydroxide, tetrapropyl ammonium hydroxide, methyltriethyl ammonium hydroxide, dimethyldibutyl ammoni-

um hydroxide, isopropyltriethyl ammonium hydroxide, diethyldihexadecyl ammonium hydroxide, dimethyldioleyl ammonium hydroxide, trimethylolcetyl ammonium hydroxide, butyltriethyl ammonium hydroxide, dibutyldicyclopentyl ammonium hydroxide, tetraheptadecyl ammonium hydroxide, tetraeicosyl ammonium hydroxide, dimethyldibenzyl ammonium hydroxide, triethyltolcetyl ammonium hydroxide, trimethylcyclohexyl ammonium hydroxide, and the like. Quaternary ammonium hydroxides having aliphatic substituent groups, dimethyldioleyl and methyltri-
oleyl ammonium hydroxides for example, have been found particularly effective for purposes of the invention and are preferred. Such ammonium hydroxides will be referred to hereafter at tetraaliphatic ammonium hydroxides.

The quaternary ammonium hydroxides useful in the preparation of the additives of the invention also include mixed quaternary ammonium compounds derived from naturally occurring materials such as coconut oil, tallow fat and soybean oil. One such material, for example, is trimethylsoya ammonium hydroxide, one aliphatic radical of which is derived from soy bean oil and which consists of a mixture of trimethyl mono-long-chain-alkyl ammonium hydroxides wherein the long chain alkyl groups consists of about 8% C₁₆ radicals, about 91% C₁₈ radicals and about 1% C₂₀ radicals. Similar mixed compounds may be derived from other naturally-occurring materials and will be familiar to those skilled in the art. Quaternary ammonium hydroxides having one or more such mixed groups are generally less expensive than the single compounds and will, in many cases, be preferred for use in accordance with the invention.

The quaternary ammonium salts of alkylenediamine tetracarboxylic acids prepared as described above are added to combustible organic liquids boiling in the range between about 75° F. and about 750° F. in accordance with the invention in concentrations ranging between about 0.0001% to about 1% by weight. Concentrations between about 0.001% to about 0.05% by weight are effective for most purposes and will generally be preferred. It will be recognized, however, that the concentration employed will depend somewhat upon the particular quaternary ammonium salt utilized, since the effectiveness of the salts varies with variations in the number of quaternary ammonium substituents present.

The combustible organic liquids in which the additives of the invention may be employed advantageously are those boiling in the range between about 75° F. and about 750° F. and include hexane, heptane, bromobenzene, turpentine, diethyl ether, toluene, petroleum naphth, xylene, gasoline, aviation turbo-jet fuel, kerosine, carbon disulfide, and the like. The additives are particularly useful in gasoline, aviation turbo-jet fuel, kerosine, diesel fuel and similar petroleum distillate fuel products. Gasolines which may be benefited by the presence of the additive include both motor gasolines and aviation gasolines such as those defined by ASTM Specifications D-910-56 and D-439-56T. Aviation turbo-jet fuels in which the additives of the invention are particularly useful are described at length in U.S. Military Specifications MIL-F-5616, MIL-F-5624D, MIL-F-25558A and MIL-F-25524A. Diesel fuels as referred to in connection with the invention are defined in ASTM Specification D-975-53T.

If desired, the additive agents of the invention may be incorporated into petroleum distillate fuels in the form of an additive concentrate containing the quaternary ammonium salts of alkylenediamine tetracarboxylic acids in combination with other additives conventionally used in such fuels. Such conventional additives include rust inhibitors, dyes, dye stabilizers, anti-oxidants, and the like. An organic solvent such as benzene, xylene, toluene, diethylene glycol, pyridine, turbo-jet fuel, or the like may be used as the vehicle in such a concentrate.

The exact nature and objects of the invention may be more fully understood from the following examples.

EXAMPLE 1

Quaternary ammonium salts of ethylenediamine tetracarboxylic acid were prepared by reacting samples of the acid with dimethyldioleyl ammonium hydroxide and trimethylsoya ammonium hydroxide in varying amounts. In each case the ammonium hydroxide was added to the ethylenediamine tetracarboxylic acid in benzene, with stirring, in a flask equipped with a condenser and a water trap. After the addition had been completed, the reaction mixture was distilled until all of the water had been removed. Benzene was evaporated to obtain the reaction products. In this manner, the following salts were obtained; the mono-dimethyldioleyl ammonium salt of ethylenediamine tetracarboxylic acid, the di-dimethyldioleyl ammonium salt of ethylenediamine tetracarboxylic acid, the tri-dimethyldioleyl ammonium salt of ethylenediamine tetracarboxylic acid, the tetra-dimethyldioleyl ammonium salt of ethylenediamine tetracarboxylic acid, the mono-trimethylsoya ammonium salt of ethylenediamine tetracarboxylic acid and the tetra-trimethylsoya ammonium salt of ethylenediamine tetracarboxylic acid.

EXAMPLE 2

In order to demonstrate the effectiveness of the quaternary ammonium salts of ethylenediamine tetracarboxylic acid prepared as described in the preceding example, tests were carried out to determine the specific conductivity of samples of aviation turbo-jet fuel and samples of the same fuel containing the salts as additives. The fuel employed in these tests was typical of the fuels designated as JP-4 aviation turbo-jet fuels which are defined by U.S. Military Specification MIL-F-5624D. It had an API gravity of about 48.7°, a Reid vapor pressure of about 2.5 p.s.i. and a boiling range between about 100° to about 520° F.

The tests were carried out by applying a fixed, direct-current voltage across a standard conductivity cell containing the sample to be tested. A standard high-resistance element was connected in series with the cell and the current which flowed in the circuit during the test was computed by measuring the voltage across the resistance element and applying Ohm's law. The resistance of the sample, the specific resistance and the specific conductivity were in turn computed. A commercially-marketed anti-static additive was tested in the same manner for purposes of comparison. The results of these tests are shown below for the base fuel and for the samples of the base fuel containing the various additives.

Table I

EFFECT OF ADDITIVES UPON ELECTRICAL CONDUCTIVITY

Additive in JP-4 Fuel	Specific Conductivity σ , mho/cm.	Ratio σ (Base + Additive) to σ Base
None.....	3.4×10^{-14}	-----
0.01 wt. percent of Mono-Dimethyldioleyl Ammonium Salt of Ethylene-Diamine Tetracarboxylic Acid.....	2.1×10^{-11}	618
0.01 wt. percent of Di-Dimethyldioleyl Ammonium Salt of Ethylene-Diamine Tetracarboxylic Acid.....	1.9×10^{-11}	559
0.01 wt. percent of Tri-Dimethyldioleyl Ammonium Salt of Ethylene-Diamine Tetracarboxylic Acid.....	2.3×10^{-11}	676
0.01 wt. percent of Tetra-Dimethyldioleyl Ammonium Salt of Ethylene-Diamine Tetracarboxylic Acid.....	1.1×10^{-11}	324
0.01 wt. percent of Mono-Trimethylsoya Ammonium Salt of Ethylene-Diamine Tetracarboxylic Acid.....	2.0×10^{-12}	95
0.01 wt. percent of Tetra-Trimethylsoya Ammonium Salt of Ethylene-Diamine Tetracarboxylic Acid.....	6.6×10^{-12}	194
0.01 wt. percent of Commercial Anti-Static Additive Marketed for Use in Distillate Fuels.....	7.2×10^{-13}	21

The data in Table I above demonstrate that the quaternary ammonium salts of alkylenediamine tetracarboxylic acids produce marked increases in the specific conductivity

ties of combustible organic liquids when added to such liquids in low concentrations. Under the same test conditions the commercial anti-static additive was found much less effective in reducing conductivity than the additives of the invention. It will be noted that the increased conductivity was particularly striking in the fuel samples containing the mono-, di-, and tri-dimethyldioleil ammonium salts of ethylenediamine tetraacetic acid. Lesser, but nevertheless significant, increases in conductivity were obtained with the tetra-dimethyldioleil ammonium, the mono-trimethylsoya ammonium, and the tetra-trimethylsoya ammonium salts of ethylenediamine tetraacetic acid. The increased conductivity of combustible organic liquids containing these additive agents makes them much less likely to accumulate electrical charges to the point that an explosion may occur than are similar liquids not containing the additives.

EXAMPLE 3

Experience has shown that the specific conductivity of an organic liquid, although it is generally an excellent indication of the tendency of a liquid to generate and accumulate electrical energy during handling and storage, is not the sole criterion for determining the effectiveness of an additive agent. A few materials which increase the specific conductivity of liquids may, in low concentrations, actually promote electrical discharges during pumping and handling of the liquids.

In order to demonstrate further the effectiveness of the additives of the present invention for their intended purpose, other tests were carried out wherein samples of aviation turbo-jet fuel containing various additive agents were circulated through glass wool to produce electrical charges which were measured. The fuel was continuously recirculated from the bottom of a stainless steel vessel employed as a sump, through a pump, and thence through a one inch stainless steel pipe containing a four gram plug of Pyrex glass wool. After passing through the glass wool, the fuel was returned to the sump. The sump was insulated from the ground. The amount of charge carried by the circulating fuel from the glass wool into the sump was measured with a micro-microammeter. A condenser surrounding the pipe connecting the bottom of the sump with the pump was employed for purposes of temperature control. Additional details concerning the test method and apparatus employed may be found in a paper by D. T. Rogers, J. P. McDermott and J. C. Munday entitled "Theoretical and Experimental Observations of Static Electricity in Petroleum Products" which appeared in Proceedings of the American Petroleum Institute, volume 37, section III, at page 44. This test has been found to be an extremely accurate method for measuring the tendency of liquids to generate and accumulate electrical charges.

The data obtained in the test described above, together with similar data obtained with the base fuel and with the base fuel containing additives suggested by the prior art are set forth in Table II below.

Table II
PRO-STATIC TENDENCY OF ADDITIVES

Additive in JP-4 Fuel	Conductivity mho/cm.	Current Amperes $\times 10^8$	Charge Remaining After $\frac{1}{2}$ Second Relaxation	Comparison With Base JP-4 percent Improvement
None	1.0×10^{-13}	3	2.25	0
0.002 wt. percent of Mono-Dimethyldioleil Ammonium Salt of Ethylenediamine Tetraacetic Acid	1.5×10^{-12}	10	0.146	93.5
0.001 wt. percent of Commercial Antistatic Additive Marketed for Use in Distillate Fuels	1.6×10^{-12}	200	2.18	3.1

Although the addition of 0.002 wt. percent of the mono-dimethyldioleil ammonium salt of ethylenediamine tetraacetic acid increased current generation slightly over the base case it may be seen that after a short ($\frac{1}{2}$ second) relaxation time, the charge remaining in the additive blend was substantially less. The third column shows the charge remaining in the liquid after one-half second relaxation time calculated from the classical relaxation formula. The fourth column shows the relative improvement over the base stock. Thus the additive blend showed a 93.5% improvement over the base fuel. On the other hand, the blend of a commercial additive having about the same specific conductivity showed only a 3.1% improvement.

EXAMPLE 4

To still further demonstrate the effectiveness of the additive agents of the invention and to point out the effect of variations in additive concentrations, tests were carried out wherein the specific conductivities of an aviation turbo-jet fuel similar to that employed in Examples 2 and 3 and samples of the same fuel containing from 0.001 wt. percent to 0.05 wt. percent of the mono-dimethyldioleil ammonium salt of ethylenediamine tetraacetic acid were measured. The results of these determinations are set forth in Table III.

Table III

EFFECT OF ADDITIVE CONCENTRATION
UPON ELECTRICAL CONDUCTIVITY

Concentration of Mono-Dimethyldioleil Ammonium Salt of Ethylenediamine Tetraacetic Acid in JP-4 Jet Fuel, weight percent	Specific Conductivity σ mho/cm.	Ratio σ (Base $\times$ Additive) To σ Base
None	5.0×10^{-14}	56
0.0010	2.8×10^{-12}	120
0.0025	6.0×10^{-12}	180
0.004	9.0×10^{-12}	260
0.005	1.3×10^{-11}	460
0.01	2.3×10^{-11}	2,000
0.05	1.0×10^{-10}	

The data in the above table show that the use of from 0.001 wt. percent to 0.05 wt. percent of the mono-dimethyldioleil ammonium salt of ethylenediamine tetraacetic acid resulted in an increase in the specific conductivity of the base fuel of from 56 to 2000 fold. The increase varied in direct proportion to the amount of the additive agent used. Since combustible liquids having specific conductivities greater than about 1.0×10^{-12} mhos per centimeter present much less of a hazard than those having lower conductivities, the use of the additive in concentrations as low as 0.001 wt. percent was effective. In liquids having a higher initial conductivity than that of the fuel used in the above tests, even lesser amounts of the additive could be employed.

EXAMPLE 5

Small amounts of water frequently accumulate in aviation turbo-jet fuels, kerosines, solvents and similar combustible liquids during storage. The effect of additives employed in such liquids upon their water tolerance properties is therefore of primary importance. It has been found that many of the additives suggested as useful for increasing the conductivity of combustible organic liquids in the past are highly surface-active materials which have an extremely adverse effect upon water tolerance. The benefit of the increased conductivity brought about through the use of such additives may largely be offset as a result of this tendency to promote the suspension of dispersed water.

In order to determine the effect of the quaternary ammonium salts of ethylenediamine tetraacetic acid on the water tolerance of combustible organic liquids to which

they are added, water tolerance tests were carried out in accordance with the method described in Federal Test Standard No. 791, Method 3251.6, "Interaction of Water and Aircraft Fuel." In brief, this test comprises agitating 80 cc. of the fuel to be tested with 20 cc. of water for a 2-minute period and then allowing the water to settle for 5 minutes. At the end of the settling period, the condition of the water-fuel interface is noted. The interface rating is assigned as follows.

INTERACTION OF WATER AND AIRCRAFT FUELS
[Method 3251.6, Fed. Test Std. No. 791]

Appearance of interface:	Interface rating
Clear and clean-----	1
A few small clear bubbles covering not more than 50% of the interface-----	1b
Shred of lace and/or film at interface-----	2
Loose lace and/or slight scum-----	3
Tight lace and/or heavy scum-----	4

The condition of the fuel layer and the water layer on either side of the interface is also noted. An interface rating of 1 or 1b, with no sign of haze or emulsion in the fuel or water layer, is a passing rating and meets the requirements of the military specifications governing the water tolerance of aviation turbo-jet fuels. The results obtained in tests of the additives of the invention and additives representative of the prior art are shown in Table IV.

Table IV

WATER REACTION OF ADDITIVES

Additive in JP-4 fuel:	Interface rating
None-----	1
0.01 wt. percent of mono-dimethyldioleyl Ammonium salt of ethylenediamine tetraacetic acid-----	1b
0.01 wt. percent of trimethylsoya ammonium oleate-----	4
0.01 wt. percent of dimethyldicoco ammonium oleate-----	4
0.01 wt. percent of 50/50 mixture of Ca salt of petroleum sulfonic acid plus K salt of P ₂ S ₅ treated polybutene-----	4
0.01 wt. percent of commercial anti-static additive marketed for use in distillate fuels-----	4

It can be seen from the results set forth in the above table that the additive agents of the invention do not reduce the interface rating below the acceptable level of 1b. The additives thus meet the critical water tolerance requirements for aviation turbo-jet fuel. The prior art material, on the other hand, gave a rating which clearly disqualifies it for use in such fuels.

EXAMPLE 6

A further critical requirement imposed upon additives employed in turbo-jet aviation fuels, gasolines, kerosines and similar materials is that they not be extracted from the material upon contact with small amounts of water normally present in storage tanks, pipe lines and the like. Tests were carried out to determine the effect of water extraction on the additives of the invention and additives suggested in the prior art by measuring the specific conductivity of samples of a turbo-jet fuel containing the additives both before and after water extraction. A reduction in specific conductivity following water extraction would indicate that substantial amounts of the additive were extracted by the water. The extraction test involved the agitation of 80 cc. of the fuel and 20 cc. of water for 2 minutes, after which the samples were allowed to stand overnight. The fuel which separated from the water was

decanted and tested for specific conductivity as described in Example 2. Results of these tests are shown in Table V.

Table V

WATER EXTRACTABILITY OF ADDITIVES

Additive in JP-4 Fuel	Conductivity, mho/cm.	
	Initial	Water Washed
None-----	4.0×10 ⁻¹⁴	6.0×10 ⁻¹⁴
0.01 wt. percent of Mono-Dimethyldioleyl Ammonium Salt of Ethylenediamine Tetraacetic Acid-----	2.1×10 ⁻¹¹	4.6×10 ⁻¹¹
0.0005 wt. percent of Commercial Antistatic Additive Marketed for Use in Distillate Fuels-----	2.0×10 ⁻¹¹	1.7×10 ⁻¹²
0.01 wt. percent of 2/1 Mixture of P ₂ S ₅ -Treated Ba Salt of Alkylphenol Sulfide plus Ca Salt of Petroleum Sulfonic Acid-----	5.1×10 ⁻¹²	1.8×10 ⁻¹³

It can be seen from the data in the above table that metallic salts such as calcium sulfonate and similar materials suggested for use as additives to improve the electrical properties of organic liquids in the past are readily extracted by water in the above described test. The additive agents of the invention, on the other hand, are not extracted to any appreciable degree and thus are suitable for use in fuels and other combustible liquids which frequently are contacted with water during storage and transportation.

EXAMPLE 7

A still further requirement for additives employed in turbo-jet fuels and similar fuel products is that they do not adversely affect the thermal stability of such fuel products. The thermal stability of aviation turbo-jet fuels is a particular problem in connection with the use of additives because of the extremely severe conditions to which such fuels are subjected in the heat exchangers which form a part of turbo-jet engine fuel systems. In these heat exchangers, the fuel is employed as a cooling medium and serves to maintain the lubricating oil temperature below temperatures at which thermal degradation tends to occur. As a result, the fuel temperature is often increased several hundred degrees in a matter of seconds.

Many additives satisfactory for use in heating oils and other fuels subjected to relatively mild temperature conditions cannot be employed in aviation turbo-jet fuels. The test employed to determine the effect of the additives of the invention on thermal stability is the CFR fuel coker test which is carried out in a rig closely resembling a scaled-down turbo-jet engine fuel system. The fuel is pumped from a supply tank through a screen and rotameter to an annular aluminum heat exchanger where it is heated to the test temperature. The heated fuel then passes from the heat exchanger through a sintered metal filter held at a temperature 100° F. above the fuel temperature. Fuel performance is determined by measuring the time required for the pressure drop across the metal filter to increase by 25 inches of mercury or by the pressure increase which occurs during 300 minutes, whichever occurs first (merit rating). This test has been found to give an extremely reliable indication of the stability properties of a jet fuel under actual service conditions. It is more fully described in CRC Manual No. 3, dated March 1957, of the Coordinating Research Council of the American Petroleum Institute and the Society of Automotive Engineers.

The results of tests of fuels containing the additive agents of the invention in the CFR fuel coker unit are shown in Table VI below.

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Table VI

EFFECT OF ADDITIVES ON FUEL THERMAL STABILITY

Fuel ¹	CFR Fuel Coker Test Results ²	
	Merit Rating ³	Tube Deposits ⁴
JP-4.....	870	1
JP-4+0.01 wt. percent of Mono-Dimethyldioleoyl Ammonium Salt of Ethylenediamine Tetraacetic Acid.....	900	2

¹ The base fuel was an aviation turbo-jet fuel meeting the requirements of U.S. Military Specification MIL-F-5624D and having properties similar to those of the turbo-jet fuels employed in the tests described in the previous examples.

² The tests were carried out with a preheater temperature of 400° F. and a filter temperature of 500° F.

³ Merit rating of 500 or more is passing.

⁴ Tube deposits are rated as follows:

0—No visible deposits

1—Visible haze or dulling but no visible color.

2—Barely visible discoloration

3—Light tan to peacock stain

4—Heavier than 3

A rating of 2 or less is passing.

The above data demonstrate that the additive agents of the invention do not substantially affect the thermal stability properties of the fuels to which they are added. As pointed out heretofore, this characteristic is extremely important in connection with aviation turbo-jet fuels and constitutes an outstanding advantage over additives proposed for use in the past.

EXAMPLE 8

A further characteristic of additive agents intended for improving the electrical properties of distillate fuels and similar combustible organic liquids which must be considered is the effect of changes in temperature on the action of the additive. It has been found that many additive agents, although they increase conductivity and do not produce large streaming currents at low temperatures, have strong pro-static effects at higher temperatures. The additive agents of the invention were tested to determine their effectiveness at various temperatures by measuring their pro-static tendency at temperatures of 20° F., 70° F. and 100° F. in the apparatus described in Example 3. The procedure employed was to first cool the turbo-jet fuels containing the additives from room temperature to a temperature of 20° F. and then measure their pro-static tendency. A second series of determinations was made after the fuel blends had been heated to 100° F. and a third series of measurements was carried out after the fuels has been cooled to 70° F. The results of these tests are shown in Table VII, from which it can be seen that the current obtained with the fuel containing 0.002 wt. percent of a mono-dimethyldioleoyl ammonium salt of ethylenediamine tetraacetic acid showed only a slight increase in current over the 80° F. temperature range whereas with the commercial additive tested the current at 100° F. was more than 800 times the current at 20° F. It is obvious from these data that the commercial additive is very much less effective at high temperatures than at low temperatures and that the effectiveness of the additives of the invention is substantially independent of temperature.

Table VII

VARIATION OF ADDITIVE EFFECTIVENESS WITH TEMPERATURE

Additive in JP-4 Fuel	Conductivity mho/cm.	Current, Amperes×10 ⁸		
		20° F.	70° F.	100° F.
None.....	1.0×10 ⁻¹³	4	3	3
0.002 wt. percent of Mono-Dimethyldioleoyl Ammonium Salt of Ethylenediamine Tetraacetic Acid.....	1.5×10 ⁻¹²	3	10	20
0.0003 wt. percent of Commercial Anti-static Additive Marketed for Use in Distillate Fuels.....	5.3×10 ⁻¹²	9	5,000	7,500

EXAMPLE 9

Petroleum distillate fuels and similar combustible organic liquids are frequently contacted with small amounts of water. The effect of water on the action of additives employed to improve the electrical properties of such liquids is therefore of great importance. That the inclusion of small amounts of water in fuels and similar liquids containing the additive agents of the invention does not detract from the effectiveness of those additives is shown by data obtained in a series of tests wherein the pro-static tendencies of fuels containing the additives and small amounts of water were measured. The pro-static tendencies were determined by means of the method and apparatus described in Example 3. The results of these determinations are shown in Table VIII and it can be seen that the current obtained decreased with increasing amounts of water.

Table VIII

VARIATION OF ADDITIVE EFFECTIVENESS IN PRESENCE OF WATER

Additive in JP-4 Fuel	Conductivity mho/cm.	Current at 70° F., Amperes×10 ⁸		
		0% H ₂ O	0.05% H ₂ O	0.1% H ₂ O
None.....	1.0×10 ⁻¹³	3.8	3.8	3.8
0.002 wt. percent of Mono-Dimethyldioleoyl Ammonium Salt of Ethylenediamine Tetraacetic Acid.....	1.5×10 ⁻¹²	12	7	2.2
0.0003 wt. percent of Commercial Antistatic Additive Marketed for Use in Distillate Fuels.....	5.3×10 ⁻¹²	6,000	3,500	24

EXAMPLE 10

To a gasoline boiling between 98° F. and 340° F. and having a Research Octane Number of 100.5 is added 0.007 wt. percent of a tetrabutyl ammonium salt of propylenediamine tetrapropionic acid in order to improve the electrical properties of the gasoline to reduce the danger that an explosion due to the generation and accumulation of electrical energy will occur during transportation and storage of the gasoline.

EXAMPLE 11

A diesel fuel boiling in the range between 310° F. and 620° F. and meeting the specification set forth in ASTM Specification D-975-53 contains 0.02 wt. percent of the trimethylbenzyl ammonium salt of butylenediamine tetraacetic acid as an additive for improving the electrical properties of the fuel.

What is claimed is:

1. A combustible organic liquid boiling in the range between about 75° F. and about 750° F. and having a specific conductivity in the range between about 1×10⁻¹⁵ and about 1×10⁻¹² mho per centimeter to which has been added from about 0.0001% to about 1% by weight of a quaternary ammonium salt of an alkylenediamine tetracarboxylic acid having from 2 to 4 carbon atoms in

the alkylenediamine portion of the molecule and from 2 to 4 carbon atoms in each of the carboxylic acid substituent groups, and wherein the quaternary ammonium radicals are selected from the group consisting of unsubstituted aliphatic, cycloaliphatic, and aryl radicals.

2. A composition as defined by claim 1 wherein said salt is a salt of ethylenediamine tetraacetic acid.

3. A composition as defined by claim 1 wherein said salt is an unsubstituted tetraaliphatic ammonium salt.

4. A composition as defined in claim 1 wherein said combustible organic liquid is a hydrocarbon oil.

5. A hydrocarbon oil boiling in the range between about 75° F. and about 750° F. to which has been added from about 0.0001% to about 1% by weight of an unsubstituted tetraaliphatic ammonium salt of ethylenediamine tetraacetic acid wherein the aliphatic groups each contain from 1 to about 24 carbon atoms.

6. A composition as defined by claim 5 wherein said salt is a dimethyldialiphatic ammonium salt having aliphatic groups of from about 16 to about 20 carbon atoms.

7. A composition as defined by claim 5 wherein said salt is a mono-quaternary ammonium salt.

8. A composition as defined by claim 5 wherein said salt is present in a concentration in the range between about 0.001% and about 0.05% by weight.

9. A composition as defined by claim 5 wherein said salt is a dimethyldialkenyl ammonium salt.

10. A composition as defined in claim 5 wherein said salt is a dimethyldiolel ammonium salt.

11. A composition as defined in claim 5 wherein said salt is a methyltriolel ammonium salt.

12. A petroleum distillate fuel boiling in the range between about 75° F. and about 750° F. to which has

been added from about 0.0001% to about 1% by weight of a dialkyl dialkenyl ammonium salt of ethylenediamine tetraacetic acid in which the alkenyl radicals each contain from about 16 to about 20 carbon atoms.

13. A fuel as defined by claim 12 wherein said salt is a mono-dimethyldiolel ammonium salt.

14. A fuel as defined by claim 12 wherein said salt is a di-dimethyldiolel ammonium salt.

15. A petroleum distillate turbojet fuel boiling in the range between 100° F. and 520° F. having incorporated therein from about 0.001 to about 0.05% by weight of a dialkyldialkenyl ammonium salt of an ethylene diamine tetraacetic acid.

16. A fuel composition as defined in claim 15 wherein said salt is a dimethyldiolel ammonium salt.

17. A composition according to claim 1 wherein said salt is a tetrabutyl ammonium salt of propylenediamine tetrapropionic acid.

18. A composition according to claim 1 wherein said salt is a trimethylbenzyl ammonium salt of a butylenediamine tetraacetic acid.

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