

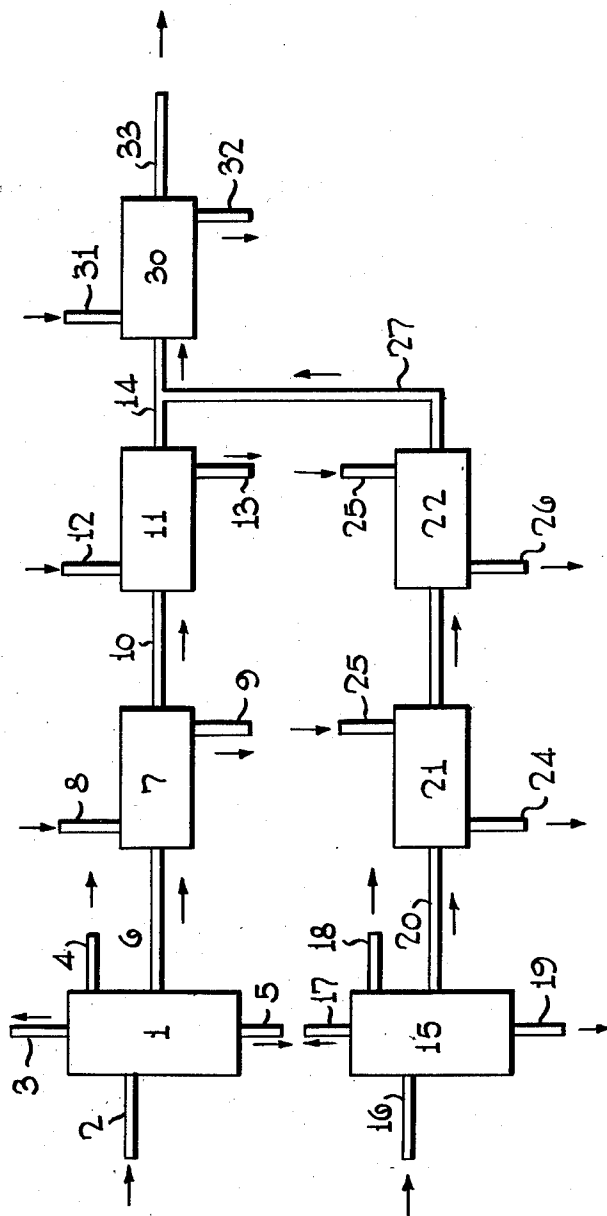
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FUEL OIL TREATED WITH ZINC

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FUEL OIL TREATED WITH ZINC

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The present invention is concerned with an improved process for the production of high quality fuel oils. It is especially directed toward the production of diesel fuels that are characterized by having low deposit-forming tendencies when utilized in diesel engines. In accordance with the present process, fuel oils and particularly those boiling in the diesel fuel boiling range, are intimately contacted with zinc under conditions whereby the deposit-forming tendencies of the resulting fuels are substantially reduced.

It is well known in the art to produce diesel fuels by various refining operations. These fuels are utilized in compression-ignition engines. In general, diesel fuels are either distillates of the gas oil type such as those boiling in the range from about 325° to 725° F., or long residua from crude oils, and have gravities in the range from about 15° API to 40° API. While these fuels in general are very satisfactory, one disadvantage of diesel fuels, particularly those of high sulfur content, is that they tend to form carbonaceous and gummy deposits when burned in the compression-ignition engine. Residual fuel oils containing sulfur compounds and/or vanadium compounds also form objectionable corrosive products in gas turbines and boiler furnaces. Various steps have been taken to overcome these disadvantages, since in time they materially lower the efficiency of operation of the equipment. For example, in the refining processes, acid treating, caustic treating, sweetening and clay filtering steps have been utilized. It has now been discovered that the deposit-forming tendencies of fuel oils can be materially lessened by treating the fuel with zinc, preferably zinc that has been finely divided. The treatment is advantageously applicable to conventionally refined diesel fuels. While the mechanics of the operation is not entirely understood, it is assumed that the effect is due to a reaction between metallic zinc and naturally occurring sulfur compounds present in the fuel and possibly to a reaction with ash-forming constituents of the fuel. Thus, a particular adaptation of the present invention is to contact a diesel fuel having a satisfactory sulfur content with zinc and a further preferred adaptation is to blend the zinc-contacted diesel fuel with other diesel fuels of relatively low sulfur content which have not been treated with zinc. Other metals of Group II of the Periodic Table of Elements, for example, magnesium, can be used, but zinc is the preferred metal. As pointed out heretofore, diesel fuels and fuel oils may be derived from petroleum by a variety of methods including straight run distillation from crude petroleum oil and thermal or catalytic cracking of petroleum oil fractions. Diesel fuels fall within A. S. T. M. specification D-975-48 T, grades 1 to 6.

The present invention may be fully appreciated by reference to the drawing illustrating one embodiment of the same. Referring specifically to the drawing, a low sulfur crude is introduced into distillation zone 1 by means of line 2. Temperature and pressure conditions are adjusted in zone 1 to remove hydrocarbons boiling below the gasoline motor fuel boiling range by means of line 3. Hydrocarbon constituents boiling in the gasoline motor fuel boiling range are removed by means of line 4 while a residuum fraction is removed by means of line 5. A fraction boiling within the diesel fuel boiling range (350° to 700° F.), is removed by means of line 6, and passed into acid treating zone 7. Acid is introduced by means of line 8 and spent acid is removed by means of line 9. The acid treated oil is removed

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by means of line 10 and passed into a caustic treating zone 11. Fresh caustic is introduced by means of line 12 while the spent caustic is removed by means of line 13. The caustic treated oil is removed from zone 11 by means of line 14 and blended with another diesel oil fraction secured as hereinafter described.

A high sulfur crude is introduced into distillation zone 15 by means of line 16. Temperature and pressure conditions are adjusted to remove low boiling hydrocarbons overhead by means of line 17. Hydrocarbons boiling in the motor fuel boiling range are removed by means of line 18, while a residuum fraction is separated by means of line 19. A high sulfur diesel oil fraction is removed by means of line 20, acid treated in zone 21 and caustic treated in zone 22. The acid is introduced into zone 21 by means of line 23, while the spent acid is removed by means of line 24. Caustic solution is introduced into zone 22 by means of line 25 and the spent caustic soda is removed by means of line 26. The treated oil is removed by means of line 27 and blended with the treated oil removed from zone 11 by means of line 14.

The blend is introduced into zone 30 wherein it is contacted at a temperature in the range from about 70° F. to 470° F., preferably at a temperature in the range from about 120° F. to 320° F., with metallic zinc. The zinc is introduced as a powder or slurry into zone 30 by means of line 31 and removed by means of line 32. Alternately zone 30 is packed with zinc turnings or with granular zinc. The zinc treated blend is removed by means of line 33 and further refined as desired. It is to be understood that zones 1, 7, 11, 30, 15, 21 and 22 may comprise any number and arrangement of stages.

As pointed out heretofore, the present invention is broadly concerned with the treatment of fuel oils with metallic zinc whereby the deposit forming tendencies of the fuels is materially decreased. For satisfactory results, the oils contacted with zinc should contain sufficient sulfur compounds. The sulfur content should be at least about 0.1% and preferably in the range of about 0.3 to 0.5%. Hydrogen sulfide and mercaptans are preferably removed by prior treatment. The sulfur concentration should be less than about 2% for satisfactory cleanliness in combustion. The preferred sulfur compounds are neutral or unreactive with bases. Disulfides are a type of neutral sulfur compounds in fuel oils of the present invention.

The process is advantageous for improving fuel, not only for combustion in diesel engines, but also for combustion in gas turbines and in boiler furnaces, where a reduction in deposit-forming and metal-corroding tendencies is desirable.

The process of the present invention may be fully understood by the following examples illustrating the same.

EXAMPLE I

A diesel fuel having the following inspections:

A. S. T. M. initial boiling point, ° F.	385
A. S. T. M. final boiling point, ° F.	659
Gravity, ° A. P. I.	32.8
Sulfur, Wt. per cent (other than H ₂ S and mercaptans)	0.35
Ash, Wt. per cent	0.003
Neutralization number	0.27
A. S. T. M. copper corrosion test	Pass

was in one operation treated with metallic copper and in another operation with metallic zinc. The procedure employed consisted in circulating the fuels in intimate contact with the metals at 130° F. temperature for several hours until sufficient reaction occurred to incorporate small amounts of the metals in the fuel. Contact time can be shortened when the temperature is increased. The rate of reaction approximately doubles when the temperature is raised 18° F. Analyses of the treated fuels showed the presence of 0.00128 wt. per cent copper in the one case and 0.0116% zinc in the other case. The ash content of the zinc-treated fuel was increased from 0.003 to 0.03 wt. per cent.

The treated diesel fuels were then run for 120 hours in engines manufactured by the Caterpillar Tractor Com-

pany (single cylinder "Caterpillar" 1A diesel test engines, Serial Numbers 1A-842 and 1A-843) using the Caterpillar 1A test procedure CRC-L-1-545. After running, the engine was inspected and the ring zone deposit demerits determined. The results of these tests are as follows:

Metal Used in Treating Diesel Fuel	Ring Zone Deposit Demerits ¹	
	Engine Serial No.	
	1A-842	1A-843
Copper.....	0.63	1.02; 0.76
Zinc.....	0.34	0.28

¹ Demerit ratings from zero to 10; zero being perfect and 10 being the worst that can be expected. The ratings separated by semicolons are for replicate tests. The higher content of ash-forming material when zinc was present was obviously not adverse for engine cleanliness.

EXAMPLE II

The zinc treated fuel described in Example I was compared in Caterpillar 1A Engine tests with the same base fuel that had been treated with iron rather than zinc. In some of the tests a lubricating oil A was used and in other tests a lubricating oil B was used. The lubricating oils had the following inspections:

	Lubricating Oil A	Lubricating Oil B
Vis./100° F. SUS.....	539.0	538.3
Vis./210° F. SUS.....	61.9	67
Viscosity Index.....	80	102
A. S. T. M. Pour, °F.....	-25	-10
Ash, Wt. Percent.....	0.35	0.48
Gravity, °API.....	26.3	28.4
Flash, °F.....	445	495

The results of these tests are as follows:

Caterpillar 1A engine tests.—Ring zone demerit¹

Fuel Treatment	Zinc	Iron	Engine Test Duration
Lubricating Oil A.....	0.47; 0.62; 0.34; 0.28	0.63; 1.02; 0.76; 0.61; 1.02	120 hours.
Lubricating Oil B.....	0.23	0.67	240 hours.
Average, using Oil A.....	0.43	0.81	

¹ Demerit ratings from zero to 10; zero being perfect and 10 being the worst that can be expected. The ratings separated by semicolons are for replicate tests. The higher content of ash-forming material when zinc was present was obviously not adverse for engine cleanliness.

From the above it is apparent that irrespective of the particular lubricating oil employed, the treatment of the diesel oil with zinc produced beneficial results, which, on the average, were twice as good as obtained without zinc treatment.

EXAMPLE III

An engine test was made using as a fuel the regular United States Army specified MIL-O-2104, diesel test fuel to which was added 0.2 wt. per cent zinc naphthenate (0.02 wt. per cent of zinc). The same lubricating oil on which the previous data of Example I have been reported was also used. In this engine test a ring zone demerit of 0.39 was obtained. The addition of zinc naphthenate to fuel tends, however, to make it less desirable or more readily emulsifiable with water encountered accidentally in storage tanks.

The treating temperatures are in the range of 70° F. to 470° F., preferably in the range from 120° to 320° F. The time of contact may vary appreciably from 10 minutes to 10 hours, according to the temperature used, but it is preferably less than one hour. Conditions should be adjusted so that the zinc concentration in the

treated fuel is in the range from about 0.005 to 0.05 weight percent of zinc by chemical analysis. A preferred concentration is in the range from about 0.0075 to 0.03 weight percent of zinc.

While the invention is concerned and directed in a preferred embodiment toward a novel and advantageous process for treating diesel fuels with zinc under conditions to produce in the treated oil a satisfactory concentration of an oil-soluble zinc compound, preferably an oil-soluble reaction product of zinc and thia-compounds present in a conventionally refined oil, it is to be understood that it is within the concept of the present invention to make suitable zinc compounds extraneously and to add these compounds in the correct concentration to the oil. Such zinc compounds are, for example, salts of sulfo-succinic acid, of organo-thiophosphoric acids, or of phenates of alkyl-phenol-sulfides, which have been described in the art of detergent and antioxidant additives for lubricating oil. Their use, however, increases the total sulfur content of the fuel, since they contain sulfur. It is well known that the higher the sulfur-content of the fuel, the greater is its deposit-forming tendency in engines. Obviously, the preferred process of the present invention produces a better and more economical fuel. Other materials, for example, rust-inhibitors, antioxidants, demulsifiers, ignition promoters, metal deactivators, suppressors of cloud-point or pour-point, oiliness agents, detergents, sludge-dispersers and neutralizers of vanadic corrosion and the like can be used in the fuels produced by the process of the present invention.

What is claimed is:

1. Improved process for the production of a fuel oil of low deposit forming tendencies which comprises treating a sulfur-containing petroleum fuel oil boiling above about 325° F. in the liquid phase with metallic zinc so as to incorporate about 0.005 to 0.05 wt. percent zinc in soluble form within the fuel oil.

2. Process as defined by claim 1 wherein the sulfur content of the petroleum fuel oil is in the range from 0.3% to 0.5% by weight.

3. Process as defined by claim 2 wherein said sulfur is present as disulfides.

4. Process as defined by claim 1 wherein the treating temperature employed is in the range from about 70° to 470° F.

5. Process as defined by claim 1 wherein the temperature of contacting is in the range from about 120° to 320° F.

6. Improved process for the production of a high quality fuel blend from a high sulfur fuel boiling above 325° F. and from a low sulfur fuel boiling in the diesel fuel boiling range which comprises contacting said high sulfur fuel in the liquid phase with metallic zinc at a temperature in the range from about 120° F. to 320° F., and blending the contacted fuel with said low sulfur fuel in proportion to obtain a fuel blend containing from about 0.005 to 0.05 percent zinc by weight.

7. A process for reducing the deposit-forming tendencies of a petroleum diesel fuel oil containing at least about 0.1% but less than about 2% of sulfur compounds that are neutral or unreactive with bases and boiling above about 325° F. which consists of contacting the fuel oil in liquid phase with metallic zinc at a temperature between 70° and 470° F. for a period of from about 10 minutes to 10 hours to secure a reaction between the zinc and constituents of the fuel oil whereby oil-soluble zinc compounds are formed within the fuel oil, and segregating the treated fuel oil including the oil-soluble zinc compounds from unreacted zinc to provide a fuel oil product containing about 0.005 to 0.5 wt. percent zinc.

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