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MOTOR FUEL

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This invention relates to gasoline-type motor fuels. It is more directly concerned with improving the cleanliness characteristics of gasolines.

In the operation of high-speed, high-output, spark-ignited, internal combustion engines, conditions are conducive for the formation of intake or induction system deposits which interfere with the efficiency of the engines when employed as prime movers for automotive installations. The induction system of an internal combustion engine comprises the intake manifold, intake valve ports, intake valve stems, intake valve tulip, etc. Deposits can form in sufficient quantities in intake manifolds and ports to deleteriously affect the flow of the fuel-air mixture to the cylinders. In other instances, the depositions on the valve elements result in the "burning" of the intake valves caused by the valves sticking in the valve guides.

It is therefore an object of this invention to beneficially modify the deposit-forming tendencies of gasoline. It is another object of this invention to provide a motor fuel additive for mitigating the formation of induction system deposits.

The formulation of a full-boiling range gasoline generally employs as the base fuel and as a major constituent a cracked gasoline produced by the catalytic or non-catalytic, thermal processing of petroleum gas-oil fractions. Various types of blending stocks such as polymer gasoline, thermal and catalytic reformate, Isomerate, alkylate, natural gasoline, etc., are admixed therewith to supplement and/or complement the properties, such as octane number, vapor pressure, etc., of the base fuel. While the olefin-free constituents such as alkylate, Isomerate, catalytic reformate, and natural gasoline are so-called "clean burning" substances, the olefinic gasolines such as cracked gasolines, thermal reformate, and polymer gasolines contain unstable materials which are relatively reactive and produce induction system deposits when employed in modern, high-speed, high-output, spark-ignited, internal combustion engines. According to this invention, it has been found that the formation of deposits in the induction system from unstable materials of this nature is reduced by incorporating small amounts of a hydrogen-treated, solvent extract obtained from the solvent refining of lubricating oils.

The solvent extract fractions which are hydrogen treated to produce the gasoline additive of this invention are obtained as products in the solvent refining phase of lubricatnig oil manufacture. By contacting a lubricating oil distillate or a deasphalted petroleum lubricating oil fraction with a selective solvent such as phenol, furfural, nitrobenzene, liquid SO_2, benzol-ketone, etc., there is produced a raffinate oil, essentially paraffinic in nature, having improved V. I. and oxidation resistance, and an extract portion, essentially aromatic in nature, containing the low V. I. constituents of the oil which have carbon and sludge-forming characteristics. Details of solvent

refining processes used in the production of lubricating oils are described in various standard works on petroleum refining engineering, e. g., Petroleum Refining Engineering, Nelson, 3rd ed., McGraw-Hill; Modern Methods of Refining Lubricating Oils, Kalichevsky, ACS Monograph #76, Reinhold. Because solvent extract fractions have inherent plasticizing characteristics, their use has been suggested for overcoming resin and varnish deposits which accumulate in the fuel induction system of an automotive engine, e. g., U. S. Patent 2,247,476. While a solvent extract fraction may have the property of mitigating the deposition of foreign accumulations in the cooler section of the induction system, e. g., intake manifold, a more critical scrutiny of the induction system shows that the deposits have merely moved from the cooler section to the hotter section and are formed around the intake valve port, stem, and tulip. According to this invention it has been found, however, that this disadvantageous effect can be ameliorated and induction system deposits substantially reduced by subjecting the extract fraction to mild treatment with hydrogen.

The instant invention will be more fully understood from the following detailed specific example of the preparation and use of hydrogen-treated solvent extract. A deasphalted, Mid-Continent lubricating oil distillate having the following characteristics:

° API gravity	27.5
SUS vis. @ 100° F	91.5
SUS vis. @ 210° F	38.0
Viscosity index	63
Color, NPA	+1½
Carbon residue, (Ramsbottom)	0.06
Flash, COC, ° F	365
Fire, COC, ° F	420
Pour, ° F	+55
Neutralization value (ASTM Des.: D974–52T)	2.4
Sulfur, percent wt	1.1

was contacted in a conventional solvent refining process with phenol at a temperature of about 125° F., employing 2.5 parts of phenol per 1 part of charge stock. In producing an 85 vis. @ 100° F., 95 V. I., neutral lubricating oil as raffinate, an extract material having the following properties was obtained:

Physical:	
API gravity	16.9
Specific grav., 60° F	0.951
Pounds/gallon	7.919
SUS viscosity—	
@ 100° F	165.5
@ 130° F	83.9
@ 210° F	41.1
NPA color	8+
Flash, ° F	375
Fire, ° F	430
Pour, ° F	+35
Total sulfur, wt. percent	2.08
Neutralization value	4.02
Chemical:	
Percent aromatics	73.2
Percent asphaltenes	Nil
Aniline point, ° F	104.9
Rostler analysis [1]:	
Percent nitrogen bases	2.0
Percent group 1 acidiffins	20.0
Percent group 2 acidiffins	51.2
Percent saturated hydrocarbons	26.8

[1] I. & E. Chem. 43 (3) 598.

DISTILLATION RANGE

Percent Distilled	Temperature ° F. (760 mm.)
10	695
30	704
50	709
70	718
90	727

This solvent extract fraction was treated with hydrogen at a temperature of 750° F., a pressure of 500 p. s. i. g., a liquid volume hourly space velocity of 2.2, and a hydrogen rate equivalent to 2500 ft.^{3}/bbl. (STP), in the presence of a hydrogenation catalyst comprising 9% molybdenum oxide supported on an alumina carrier. The product had the following characteristics:

Gravity, ° API	19.3
Refractive index, N^{20}_D	1.5275
Refractivity intercept $n_D^{20}-\frac{1}{2}D_4^{20}$	1.0602
Color, ASTM (NPA)	3
Total sulfur, wt. percent	1.43
Neutralization value	<0.03

The deposit-forming tendencies of gasolines containing a major portion of an olefinic gasoline were evaluated utilizing a Lauson H–2 single cylinder engine. The engine was equipped with a heated tubular glass manifold section maintained at 125° F. Temperatures were measured on the outside of the tube by an unshielded thermocouple. Current input to the heater generally was around 2 amperes. Intake manifold deposits were accumulated during a 12-hour run employing the following engine operating conditions:

Air-fuel ratio	13.8
Dynamometer load-watts	500
R. P. M	1500
Jacket temp., ° F	212
Manifold temp., interior, ° F	165
Manifold temp., exterior, ° F	315
Sump temp., ° F	140
Carburetor air temp., ° F	100
Fuel consumption, cc./min	10

After each test, the manifold was removed from the engine, and the amount of the manifold deposits determined by weighing the manifold on a suitable balance. The engine numerical rating was determined by visually evaluating the condition of intake system, comprising the intake valve port, intake valve stem, intake valve tulip, and combustion chamber.

In the demerit rating system used on the Lauson test the reference fuel is given a rating of twenty total points. This provides a value of 5 for normal deposits on engine parts and lighter deposits receive lower ratings, with 0 for clean parts. Heavier than normal deposits are demerited by increasing the rating in steps of 5 which will overshadow any clean engine part ratings and result in a greater than normal total rating.

In Table I is summarized the test results obtained by means of the Lauson test which clearly demonstrate the advantages that are obtained in mitigating induction system deposits. In interpreting the data, increased weights and increased ratings denote adverse results. The hydrogen-treated extract and untreated extract were prepared in accordance with the foregoing example.

Table I

LAUSON TEST RESULTS

Fuel	Run No.	Manif. Deposits, Gms.	Engine Numerical Rating				
			Port	Stem	Tulip	Chamber	Total
Regular Gasoline [1]	BS42	.1032	2	2	3	5	12
	1208	.1146	2	2	2	5	11
	1209	.1464	2	2	2	5	11
	1210	.1214	2	2	2	5	11
Average							
Regular Gasoline,[1] 10 ml./gal. solvent extract fraction	BS43	.018	5	5	10	5	25
	1211	.044	5	4	5	5	19
	1212	.017	4	4	10	5	23
	1213	.026	5	4	5	5	19
Average		.026	5	4	8	5	22
Regular Gasoline,[1] 10 ml./gal. Hydrogen-treated solvent extract	BS44	.020	3	3	4	5	15
	1214	.044	3	2	3	5	13
	1215	.022	5	2	3	5	15
	1216	.028	5	2	3	5	15
Average			4	2	3	5	14

[1] A conventional gasoline motor fuel containing 80 vol. % of olefinic gasolines to provide a composition having the following properties:

°API Gravity	61.5
ASTM Distillation Range—	
10 percent	135° F.
50 percent	215° F.
90 percent	325° F.

From this it is seen that while untreated as well as hydrogen-treated solvent extract were instrumental in reducing the manifold deposits by 75–80%, the untreated solvent extract fraction had a severe deleterious effect on the engine numerical rating. While a slight increase in the engine numerical rating occurs when the hydrogen-treated solvent extract is incorporated in the gasoline, it is still well under the rating obtained using the untreated solvent extract fraction and comparable with the untreated solvent extract fraction-free gasoline.

For the purposes of this invention, the solvent extract fraction which is hydrogen-treated to provide the induction system deposit-inhibitor of this invention is that aromatic hydrocarbon-containing fraction obtained in the solvent refining processing of a petroleum oil fraction with a selective solvent to produce a mineral lubricating oil of substantially improved V. I. and increased resistance to oxidation. Because of the factors involved in refining oils with selective solvents to produce a raffinate fraction of a desired quality, the properties of extract fractions will vary somewhat depending upon the feed stock, solvent, and conditions.

The solvent extract fractions which are hydrogen-treated to produce the gasoline additive of this invention will have an aromatic hydrocarbon content of about 70 to 95% by weight, a boiling range of 600°–800° F., an API gravity in the range of 10°–20°, and a refractivity intercept (J. F. I., November 1936, page 563) of not less than 1.0525. In producing solvent extract fractions having these characteristics, lubricating oil stocks obtained from Pennsylvania, Mid-Continent, Gulf Coast and other crude petroleum oil sources can be used, although Mid-Continent or Gulf Coast crudes are preferred because they are more aromatic in nature. Generally, solvent-to-oil ratios of 1 to 3 to 1 will produce extracts of desired properties; however, the selected ratio used will

depend upon the solvent employed. It is preferred that extract fractions from the production of neutral lubricating oils be employed; however, bright stock extract fractions can be employed if destructively hydrogen-treated to reduce average boiling range. Examples of suitable extract fractions are tabularly summarized in Table II.

Table II

PHYSICAL PROPERTIES OF SOLVENT EXTRACT FRACTIONS SUITABLE FOR HYDROGEN TREATING

	Light Neutral	Medium Neutral	Bright Stock
API Grav.	17.3	10.8	14.0
SUS Vis. @ 100° F.	165.5	1327	27,000
SUS Vis. @ 210° F.	41.1	65	369
NPA Color	3½ Dilute	+3 Dil.	5 Dil.
Flash, ° F.	375	415	530
Fire, ° F.	430	490	595
Pour, ° F.	+35	+35	+65
Percent Aromatics	75	85	90
Distillation Range, ASTM:			
10%	695	730	mostly above 900° F.
50%	709	795	
90%	727	835	

The hydrotreating conditions employed are:

	Range	Preferred
Temperature, ° F.	500–950	600
Pressure, p.s.i.	100–500	250
Hydrogen rate, S. C. F. H_2/bbl.	300–5,000	2,200
Liquid Volume Hourly Space Velocity	1–10	2.0

Milder temperature conditions are used when hydrogen-treating the solvent extract fraction obtained from the manufacture of low and medium viscosity, neutral, petroleum lubricating oils. The extract fractions obtained from the manufacture of high viscosity neutrals and bright stock are too heavy for best results and consequently must be cracked under mild conditions to reduce the average molecular weight. This may be done while hydrotreating by operating under more severe conditions, that is, at higher temperatures. Other conditions are essentially the same but the temperature is raised to the range of 825–950° F., preferably 875° F. Although the hydrofining conditions do not reduce the sulfur content appreciably, there is, nevertheless, some reduction of sulfur by decomposition to hydrogen sulfide. The hydrofined product must be stripped free of hydrogen sulfide. To promote the efficiency of the reaction, typical prior art hydrogenation catalysts can be employed. Hydrogenation catalysts comprising oxides or sulfides of groups VI and VIII metals are particularly useful, e. g., nickel, cobalt and iron as metals or oxides, nickel tungstate, cobalt molybdate, chromium, molybdenum and tungsten oxides or sulfides, etc. The catalysts are preferably distributed on or incorporated in a porous carrier such as activated alumina, silica gel, various siliceous cracking catalysts including SiO_2—Al_2O_3, SiO_2—ZrO_2,

$$SiO_2—Al_2O_3—ThO_2$$

etc. In the course of hydrogen-treating these conventional hydrogenation catalysts will lower the neutralization value of the solvent extract fraction. To obtain optimum results it is preferred that hydrogenation catalysts be used which will reduce the neutralization no. (1948) to less than 0.5 as a concomitant result in the hydrogen treating of the solvent extract fraction feed. Best results are obtained when the hydrogen-treated solvent extract have a neutralization value (1948) of less than 0.03. Specific conventional hydrogenation catalysts which will effect this maximum reduction include: MoO_3 on alumina where the alumina is prepared from aluminum sulfate in a conventional manner, nickel molybdate on alumina and silver molybdate on alumina, and others which function in this manner.

The amount of hydrogen-treated extract fraction to be used will vary, depending upon the amount of olefinic gasolines present in the finished motor fuel. Accordingly, the optimum amount should be determined experimentally. In general, about 10 to 50#/1000 bbls., based on the total gasoline component of the finished fuel, should be employed; however, amounts outside this range can be used.

The gasoline-type motor fuels which are beneficiated in accordance with this invention are those which contain a substantial portion of olefinic distillates boiling in the gasoline range. In general, amounts between about 5 to 100 vol. percent of a gasoline, such as those prepared by the catalytic, or non-catalytic, thermal decomposition of a petroleum gas oil fraction; non-catalytic, thermal reforming of light petroleum distillates; or polymerization of olefinic gases, in the finished gasoline, produce undesirable induction system deposits. As has been pointed out above, other hydrocarbon blending components can be admixed with the cracked base stock. In addition, the compounded gasolines can contain other additives such as tetraethyl lead fluid, ignition improvers such as organic phosphates, esters of dibasic organic acids, antioxidants, etc. These additives can also contribute to the induction system deposit-forming tendencies of the base gasoline, a deleterious result which is also mitigated by the use of the hydrogen-treated solvent extract of this invention.

Although the instant invention has been illustrated by specific compositions which carry out the objectives of this invention, it is obvious that variations will be apparent to those skilled in the art to which this invention pertains. Accordingly, the invention is limited only by the appended claims which define and claim the subject invention as:

1. A gasoline motor fuel composition comprising a portion of an olefinic gasoline having induction system deposit-forming tendencies and an amount sufficient to mitigate the accumulation of induction system deposits of a hydrogen-treated solvent extract, said hydrogen-treated solvent extract being prepared by contacting a solvent extract fraction, obtained from the solvent refining of a lubricating oil stock with a selective solvent to produce a lubricating oil having an enhanced viscosity index and improved resistance to oxidation, with hydrogen at a temperature of about 600°–950° F., a pressure of about 100–500 p. s. i., a hydrogen rate of about 300–5000 s. c. f. hydrogen/barrel of feed, and a liquid hourly volume space velocity of about 0.5–10.0 in the presence of a hydrogenation catalyst.

2. A motor fuel composition in accordance with claim 1 in which the gasoline portion of said composition contains 5–100 volume percent of an olefinic gasoline.

3. A motor fuel composition in accordance with claim 1 in which said solvent extract fraction is obtained from the manufacture of neutral petroleum lubricating oils with a selective solvent.

4. A gasoline motor fuel composition comprising a gasoline base containing 5–100 volume percent of an olefinic gasoline having incorporated therein an amount of an hydrogen-treated, solvent extract fraction sufficient to mitigate the accumulation of induction system deposits, said hydrogen-treated solvent extract being prepared by contacting a solvent extract fraction containing 70–90 wt. percent of aromatic hydrocarbons, said fraction being obtained from the solvent refining of a petroleum lubricating stock with a selective solvent to produce a lubricating oil having an enhanced V. I. and improved resistance to oxidation, with hydrogen at a temperature of about 600–950° F., a pressure of about 100–500 p. s. i., a hydrogen rate of about 300–5000 s. c. f. hydrogen/barrel of feed, and a liquid hourly volume space velocity of about 0.5–10.0 in the presence of a hydrogenation catalyst.

5. A gasoline motor fuel composition in accordance with claim 4 having incorporated therein 10–50 pounds

per one thousand barrels of gasoline base of a hydrogen-treated solvent extract to mitigate the accumulation of induction system deposits.

6. A composition in accordance with claim 4 in which said hydrogen treated extract has a neutralization value of less than about 0.5.

7. A gasoline motor fuel composition comprising a gasoline base containing 5–100 volume percent of a cracked gasoline having induction system deposit-forming tendencies having incorporated therein 10–50 pounds per one thousand barrels of gasoline base of a hydrogen-treated solvent extract having a neutralization value of less than 0.3 to mitigate the accumulation of induction system deposits, said hydrogen-treated solvent extract being prepared by contacting a solvent extract fraction obtained from solvent refining of a lubricating oil stock to produce a lubricating oil having enhanced viscosity index and improved oxidation resistance, having the following characteristics: ASTM boiling range (10%–90%) of 695°–727° F., °API gravity 16.9, 73.2 wt. percent aromatics, said fraction being obtained from the manufacture of a Mid-Continent neutral petroleum lubricating oil, with hydrogen at a temperature of about 750° F., a pressure of about 500 p. s. i. g., a liquid hourly space velocity of 2.2 and a hydrogen rate of about 2500 ft. cu./barrel (STP) in the presence of a hydrogenation catalyst comprising 9% molybdenum oxide supported on an alumina carrier.

8. A gasoline, motor fuel additive comprising a hydrogen-treated, solvent extract prepared by contacting a solvent extract fraction having an ASTM boiling range of 600°–950° F., an API gravity of 10°–20° API, an aromatic hydrocarbon content of about 70–95% by weight and a refractivity intercept of not less than about 1.0525, obtained from the solvent refining of a lubricating oil stock with a selective solvent to produce a lubricating oil having an enhanced viscosity index and improved resistance to oxidation, with hydrogen at a temperature of about 600–950° F., a pressure of about 100–500 p. s. i., a hydrogen rate of about 300–5000 s. c. f. hydrogen/barrel of feed, and a liquid hourly volume space velocity of about 0.5–10.0 in the presence of a hydrogenation catalyst.

9. A gasoline, motor fuel additive comprising a hydrogen-treated, solvent extract having a neutralization value (ASTM Designation D974–52T) of not more than 0.03 prepared by contacting a solvent extract fraction having an ASTM boiling range of 600°–950° F., an API gravity of 10°–20° API, an aromatic hydrocarbon content of about 70–95% by weight and a refractivity intercept of not less than about 1.0525, obtained from the solvent refining of a lubricating oil stock with a selective solvent to produce a lubricating oil having an enhanced viscosity index and improved resistance to oxidation, with hydrogen at a temperature of about 600–950° F. a pressure of about 100–500 p. s. i., a hydrogen rate of about 300–5000 s. c. f. hydrogen/barrel of feed, and a liquid hourly volume space velocity of about 0.5–10.0 in the presence of a hydrogenation catalyst selected from the group consisting of molybdena on alumina, nickel molybdate on alumina, and silver molybdate on alumina.

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