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MOTOR FUEL COMPOSITION CONTAINING SILICA GEL-EXTRACTED BRIGHT STOCK

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The present invention relates to improved motor fuels and methods for making them, and more particularly to motor fuels containing additive agents adapted to reduce or prevent gum problems in the motor while simultaneously lubricating the moving parts in the upper part of the motor. More particularly, the present invention relates to a gasoline composition containing an improved solvent oil adapted to prevent valve stem and piston ring sticking and be a general purpose upper cylinder lubricant.

The use of solvent oils in gasoline composition to control these problems and provide upper cylinder lubrication has long been known. Thus, a satisfactory composition is described in U.S. Patent 2,066,234, issued to Sloane and Wasson on December 29, 1936. This patent describes solvent oils as consisting of a liquid hydrocarbon mixture having a 50% distillation point above 350° F. at 10 mm. Hg pressure, having a Saybolt viscosity at 100° F. not above 450 seconds, and having an A.P.I. gravity of about 18 to 28°. A typical solvent oil, for example, has the following inspections:

50% distillation point	413 @ 10 mm. Hg
Saybolt viscosity at 100° F.	75.3
A.P.I. gravity	26.6

In general, the solvent oil is present in a gasoline to the extent of from about 0.05 to 1.0%.

The need for a highly active solvent oil type additive has been long recognized. Manifold deposit and intake valve (particularly underside) deposite buildup represents a serious fuel deficiency, particularly when the fuel is used in low temperature service with considerable engine idling time. Catalytically cracked gasolines which have comparatively high octane numbers and are thus widely used are unstable and require the use of an antioxidant. Both these unstable fuels and antioxidant residues contribute to manifold and intake valve deposits. Use of a solvent oil type additive represents a desirable method of minimizing these deposits. However, solvent oils of the Sloane-Wasson type, while controlling manifold deposits, are not effective in reducing underside intake valve deposits. The accumulation of these latter deposits under high mileage can cause severe engine operating conditions.

It has now been found that an excellent motor and aviation gasoline solvent oil may be provided by incorporating in the gasoline, from 0.1 to 1.0% by weight of a bright stock which has been silica gel extracted to an aromatics content of less than about 5%. More particularly, this invention is based on the surprising discovery that by select silica gel treatment of a deasphalted, solvent extracted, virgin residual oil or bright stock, a solvent oil is obtained that: (1) overcomes the problem of intake valve underside deposits to a greater degree than conventional bright stocks and other solvent oils, (2) does not contribute to Octane Requirement Increase (O.R.I.). While it is realized that very high viscosity oils might also be effective, none have been found which would not contribute to O.R.I.

Other methods of highly refining bright stocks, such as acid treatment, extensive solvent treatment, or aluminum chloride contacting, do not yield equivalent materials. The reason why silica gel treatment results in such an excellent solvent oil is not clearly understood at this time. It is postulated that the silica gel is extremely selective to the removal of aromatics and non-hydrocarbons, both of which contribute to instability and Octane Requirement Increase. Further, the remaining hydrocarbons have better solvency for the deposits than the original feed. This is surprising since solvency is normally associated with aromatics, thus indicating that the treatment leaves some materials in the bright stock in the proper amount, i.e., not too much or too little, that exhibit the desired solvency action in a solvent oil composition.

The silica gel treated bright stock of this invention can be obtained from any convenient crude source. It is much preferred to use as a starting material paraffinic crudes such as North Louisiana and Panhandle. With crudes other than paraffinic crudes, the treating steps described below result in a substantial loss in yield.

The crude is first treated by simple vacuum distillation to obtain a residual fraction boiling about 950° F. The residual fraction is then at least deasphalted and dewaxed before the silica gel treatment. It is much preferred, however, to also solvent extract the residual fraction before the dewaxing treatment. In some instances the dewaxing step can occur after silica gel treatment, but it is much preferred to carry this out before silica gel treatment and after the deasphalting and solvent extraction steps.

The residual fraction obtained by vacuum distillation is first treated by deasphalting. Any conventional means of deasphalting can be used. It is preferred to treat the residual fraction with light paraffins such as propane and butane, or mixtures thereof, at temperatures in the range of 100° to 160° F. and at solvent/oil ratios in the range of 400 to 1200%. The residual fraction is treated to obtain a material having a viscosity at 210° F. in the range of 200 to 250 S.S.U. and a Conradson carbon content of less than 1 wt. percent. For the preferred paraffinic residual fractions, the yields are in the range of 40 to 70 wt. percent.

In a preferred embodiment, the deasphalted fraction is then subjected to solvent extraction employing any conventional solvent such as phenol, furfural, sulfur dioxide, ammonia, nitrobenzene, etc. The extent of the solvent extraction is such as to obtain a material having a V.I. above 100, which reflects the reduction in aromatic content, and a viscosity in the range of 100 to 150 S.S.U. at 210° F. The yields are in the range of 50 to 80 wt. percent based on feed to the extraction step.

In the dewaxing step, the deasphalted residual fraction, which is also preferably solvent extracted as indicated above, is treated to remove the paraffins and to lower its pour point to at least below +30° F. The yield obtained depends upon the wax content of the fraction and is usually in the range of 70 to 90% for paraffinic type residual oils. Conventional dewaxing techniques can be used, solvent dewaxing being preferred. In this method, the residual fraction is contacted with about 2 to 4 parts per volume with a solvent such as propane or methyl-ethyl-ketone. The mixture is then heated to assure solution of the wax, and is then chilled to about 25 to −10° F. to obtain crystallization. The mixture is then filtered or centrifuged to remove the wax.

The bright stock so obtained by the deasphalting and dewaxing steps may then be further treated as desired, such as by decolorizing, as by clay contacting, although this is not necessary because the silica gel treatment accomplishes about the same results.

The bright stock is then treated specifically with silica gel to obtain the desired material to add to gasoline compositions. As discussed later (Table IV), other methods of highly refining residual fractions would not give equivalent results. The silica gel treatment is well known in the art and is carried out in a conventional manner by percolating the bright stock, preferably in solution with a solvent such as heptane, through a column of silica gel. A preferred silica gel is the standard commercial 28/200 mesh manufactured by the Davison Chemical Company. It is preferred to contact the bright stock with 300 to 1600 wt. percent of the silica gel at a temperature in the range of 50° to 100° F. The silica gel can be periodically regenerated as desired by standard solvent elution, as for example, with acetone, benzene, Cellosolve, or mixtures thereof. The silica gel treatment is sufficient to reduce the concentration of single ring aromatics to below 5 wt. percent and to reduce the condensed ring aromatics to essentially negligible proportions, i.e., less than 0.01 wt. percent. By single ring aromatics are meant compounds containing a single benzene nucleus, and by condensed ring aromatics are meant compounds such as anthracene and derivatives thereof, both as determined by spectographic analysis.

The following Table I gives the inspections of the final silica gel treated virgin bright stock that must be met in order to obtain the suitable solvent oil of this invention.

TABLE I

Viscosity at 210° F., SSU	70 to 150.
Viscosity index	100 to 120.
Conradson carbon, wt. percent	Below 0.1.
Single ring aromatics, wt. percent	Below 5.
Condensed ring aromatics, wt. percent	Nil.
Pour point, ° F.	Below +30.
Gravity, ° API	27 to 32.
Tag. Robinson color	Above 15.
Nitrogen, wt. percent	Nil.
Sulfur, wt. percent	0 to .05.
Initial boiling point	Above 850° F.
R.I. (Resinification Index)	Below 16 mg./5 gr.

It is to be noted that the bright stock used in this invention is specifically a virgin bright stock and this means one that has not been subjected to thermal or catalytic cracking conditions. The Resinification Index, which is a measure of the propensity of an oil to form deposits in a combustion chamber, i.e. contribute to O.R.I., should be low. The procedure for determining this property will be described later.

In carrying out the invention, a small amount of the described solvent oil is either added to the gasoline itself or is injected into the manifold in any desired manner in order to contact the gum-coated surface. The amount of solvent oil to be used may vary over a wide range depending upon various factors such as the type of motor fuel being used and the type of engine. In general, from 0.05 to 1.0% of solvent oil is sufficient, and preferably the amount used is between 0.10 to 0.75% by volume based on the gasoline blend.

The solvent oil composition of the present invention is also applicable to dissolving and fluxing gummy deposits from such fuel systems as diesel, heating oil, jet engines, turbines and the like. Furthermore, it may be combined with additives in motor fuels having other properties, such as dimethyl carbinol for de-icing, various anti-rust agents and the like.

Example I

A bright stock prepared in the manner previously described was tested as a solvent oil in a high octane premium gasoline. The sample was tested in 0.25% concentration in a duel fuel system Buick engine operating with premium gasoline and a 10 W-30 lubricant. The

car was run for almost 6500 miles in the test. As a comparison, various commercially available solvent oils also were tested. Solvent oil A is a propylene oxide polymer of 1100 to 1200 molecular weight. The conventional solvent oil B is a hydrofined naphthenic distillate with a viscosity of about 75 to 85 SSU at 100° F.

The particular silica gel-extracted bright stock (B.S.) employed in the test had the following inspections:

Gravity, API	31.1.
Viscosity, SSU	913 @ 100° F. 95 @ 210° F.
Conradson carbon	0.01.
Aromatics	<3.0%.
R.I. @ 67° C.	1.4598.
Sulfur	0.03%.
Nitrogen (comb.)	Nil.

The chief property examined was the relative ability of the solvent oils to keep the underside of the intake valve clean. A completely clean valve would give a 0 demerit rating and a completely fouled valve would give a 10 demerit rating. In addition, its contribution to combustion chamber deposits and its effect on octane requirement increase (O.R.I.) were measured.

TABLE II

COMPARISON OF SOLVENT OILS

[In high octane premium gasoline and using a 10 W-30 lubricating oil in a dual fuel system Buick, run about 6,500 miles]

Solvent oil (vol. percent)	Demerit	Comments
Conventional solvent oil B (0.5%).	2.5	Some spark plug fouling.
Solvent oil A (0.5%)	0.75	No spark plug fouling.
Silica gel treated bright stock (0.25%).	0.75	No spark plug fouling. Very slight surface ignition (not limiting in any way).
Conventional naphthenic bright stock (0.5%).	0.5 to 0.7	Very severe spark plug fouling.

TABLE III

DUAL FUEL SYSTEM BUICK

Oil: 10 W-30
Fuel: Premium gasoline

	Solvent oil	
	Silica gel treated bright stock	Solvent oil "A"
Solvent oil concentration, percent	0.25	0.5
Tank	Left	Right
Carburetor deposits (grams):		
Heptane soluble	0.15	0.08
Acetone soluble	0.05	0.03
Total	0.20	0.11
Manifold deposits (grams):		
Heptane soluble	0.39	0.81
Acetone soluble	1.19	0.06
Total	1.58	0.87
Combustion chamber deposits (grams)	31.80	44.66
Demerit ratings:		
Piston top	1.5	1.63
Cylinder head	1.0	1.25
Intake valve top	1.25	1.50
Exhaust valve top	2.13	1.63
Intake valve underside	[1] 0.69	0.65
Intake valve stem	0.31	0.31
Exhaust valve underside	1.50	1.13
Exhaust valve stem	1.31	1.31
Octane requirements:		
Prim. ref. fuels—		
Initial	91.1	87.1
Equilibrium	93.5	94.8
ORI	2.4	7.7
Comm. ref. fuels—		
Initial	91.0	88.4
Equilibrium	[1] 95.2/94.6	95.2
ORI	4.2	6.8

[1] Very slight surface ignition.

The data in Table II show that the use of 0.25 volume percent of silica gel bright stock in the premium gasoline was effective in reducing intake valve underside deposits in the test car, and does so in a manner superior over commercially available solvent oils. In half the concentration, the oil of the present invention did a better cleaning job than the commercially available solvent oil B. Furthermore, when a conventional bright stock, which is high in naphthenic content is employed as a solvent oil, spark plug fouling was observed, whereas the silica gel extract material did not show any spark plug fouling. It is also well known that conventional bright stocks contribute to O.R.I. As shown in Table III, the present invention (silica gel extracted bright stock) does not contribute to O.R.I.

Table III shows in detail the advantages of incorporating into a gasoline the silica gel treated bright stock over solvent oil A, which has hitherto been considered to be the most desirable type of solvent oil. In fact, solvent oil A is normally used as a target for commercial solvent oils but because of its high cost is not used commercially. The solvent oil of the present invention is substantially superior over the target.

For example, total combustion chamber deposits are lower for the silica gel treated bright stock than for solvent oil A (31.8 vs. 44.6). Furthermore, the Octane Requirement Increase is about 50% less than using the silica gel extracted bright stock.

Table IV gives a comparison of the properties of several highly refined bright stocks. A screening test to evaluate the tendency of these oils to contribute to Octane Requirement Increase is the Hydrogen Combustion Test which determines the Resinification Index referred to in Table I, page 7. The test is described in detail in U.S. Patent 2,761,766, issued September 4, 1956 to A. H. Popkin. Basically, 5 grams of oil (straight or in blend with another oil) are burned under specified conditions in a hydrogen flame until a dry residue remains. The weight of deposits for a given weight of charge defines the Resinification Index.

As shown in Table IV, the silica gel treated bright stock is superior to the other types of "super" refined bright stocks since it has the lowest resinification Index.

The phenol treated material in Column 2, Table IV, was obtained by further extracting a conventional bright stock with 300% anhydrous phenol at 200° F. in a single stage batch treat. The raffinate was stripped of phenol to a 78% yield.

TABLE IV

EFFECT OF BRIGHT STOCK REFINING ON OCTANE REQUIREMENT INCREASE TENDENCY

Process	Conventional refining plus					
	None	Phenol extraction	$AlCl_3$ W/ clay	Clay	Alumina	Silica gel
Yield, vol. percent	100	78	80	98	96	70
Gravity, ° API	26.6	28.1	28.5	26.7	27.7	31.1
Viscosity, SSU:						
At 100° F	2,209	1,784	1,126	2,068	1,376	913
At 210° F	146	133	100.2	141	118	95
Viscosity index	101	105	104	101	108	104
N_2, weight percent	0.015	0.004			0.004	Nil
S, weight percent	0.5	0.30	0.28	0.41	0.44	0.03
Conradson carbon,[1] weight, percent	0.86	0.58	0.26	0.75	0.54	0.01
Resinification index						
straight [1]	49	54	21	29	47	12
5% in a distillate motor oil	11	13	9	7	9	5

[1] Average of at least two determinations.

The material in column 3 was obtained by treating with 5% of aluminum chloride for two hours at 350° F. followed by clay treating.

The clay treated oil in column 4 was obtained by contacting the oil with "Superfiltrol" clay at 400° to 450° F. for one hour. Treat was one-half pound clay per gallon of oil. The alumina treated oils were obtained in a conventional manner by percolating the bright stock in heptane solution through Alcoa F–20 alumina at room temperature to a 96% yield.

An attempt was made to severely acid treat the bright stock with sulfuric acid. It was not possible to acid treat the heavy conventional bright stock to a reasonable yield level and produce a material even worthy of testing.

What is claimed is:

1. A fuel composition comprising light hydrocarbons boiling in the gasoline range and 0.1 to 1.0% by weight of a silica gel extracted bright stock having less than 5% aromatics content and a pour point less than +30° F.

2. The composition of claim 1 wherein said bright stock is derived from a paraffinic crude by first distilling the crude to obtain the residual fraction, deasphalting said residual fraction to obtain a material having a viscosity at 210° F. in the range of 200 to 250 SSU and a Conradson carbon content of less than 1 wt. percent, extracting the deasphalted material with a solvent to obtain a material having a viscosity index above 100 and a viscosity in the range of 100 to 150 SSU at 210° F., dewaxing the solvent extracted material to a pour point below +30° F., and treating the dewaxed material with 300 to 1600 wt. percent of silica gel to obtain said bright stock having the following characteristics:

Viscosity at 210° F., SSU	70 to 150.
Viscosity index	100 to 120.
Conradson carbon, weight percent	below 0.1.
Single ring aromatics, weight percent	below 5.
Condensed ring aromatics, weight percent	Nil.

References Cited in the file of this patent

UNITED STATES PATENTS

2,654,697 Andress et al. ---------- Oct. 6, 1953