

PATENT SPECIFICATION

NO DRAWINGS

849,889



Date of Application and filing Complete Specification June 29, 1959.

No. 22318/59.

Application made in United States of America on July 1, 1958.

Complete Specification Published Sept. 28, 1960.

Index at Acceptance:—Class 91, G1A1.

International Classification:—C10g.

COMPLETE SPECIFICATION

Fuel Composition

We, SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ N.V., a Company organised under the laws of The Netherlands, of 30 Carel van Bylandtlaan, The Hague, The Netherlands, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 The invention relates to a fuel composition for use in a spark ignition internal combustion engine, especially for such an engine having a high compression ratio.

15 Since spark ignition engines were first manufactured, the compression ratios of the engines have steadily been raised, especially in aviation and automotive engines. This has made possible greater power for the same size engine and more efficient utilization of the fuel.

20 Increased compression ratios have of course necessitated the use of fuels of increased resistance to detonation, or spark knock, and heretofore it has been possible, by the development of new hydrocarbon conversion processes, for example cracking and reforming and by

25 using antiknock agents such as tetraethyl lead, to manufacture high quality fuels fully adequate to take advantage of these advances in engine design.

30 Of the many aspects of fuel performance (such as ease of starting, vapour-locking tendency, cleanliness, odour, and combustion noise) which the manufacturer of a fuel must consider carefully, the control of combustion

35 noise is probably the most important because it indicates a reduced efficiency in utilizing available fuel energy with a resulting loss of power and mileage. In the past, control of combustion noise has been primarily a matter

40 of suppressing spark knock, but the compression ratios of the newer engines have reached a point where other related phenomena have become serious. "Wild ping", a sharp engine noise something like the noise of spark knock but occurring at random, is likely if the

45

deposits in the combustion chamber tend to glow and ignite the fuel-air mixture prematurely. Even less familiar problems now becoming prevalent include "pounding" or "high speed rumble", and "hot starting".

Pounding is an engine noise which has been described as sounding like a "broom handle dragged along a picket fence". It is encountered especially in the case of high compression engines, usually at fairly high speeds under moderate to heavy loads, and, like spark knock is aggravated by increasing the compression ratio of the engine. Unlike spark knock however, raising the octane number of the fuel will not prevent pounding. Precision measurements of high frequency pressure fluctuation in the combustion chamber have shown that pounding noise is not due to these pressure fluctuations as are the noises of spark knock and wild ping; analysis of pounding noise has shown that it involves high intensity sound in the low frequencies, especially in the 400 to 1500 cycles per second range, as compared to spark knock which is characterised by high intensity sound in the 6000 cycles per second range as well as a somewhat lesser intensity sound at about 600 cycles per second. It is possible that pounding is a vibration of power train components such as connecting rods and crank shafts caused by excessive rise in pressure during the combustion of the fuel, i.e., too rapid a burning rate. It has been found that pounding is aggravated by increasing the concentration of aromatic hydrocarbons in the fuel; this makes it likely that it will be a problem of increasing seriousness because the trend in refining processes has been toward gradually increasing concentrations of aromatics in the fuel.

"Hot starting" is another phenomenon which has been encountered only in the newer very high compression engines. This is a noise like spark knock which occurs when restarting a warm engine. Engine block and compression heat, the presence of deposits, the

slow piston travel during cranking, and the susceptibility of the fuel to spontaneous ignition all bring about an untimely ignition of the fuel-air mixture under such conditions that this mixture detonates.

Many fuel quality characteristics besides the avoidance of combustion irregularities have also recently become more critical. For example the fuel should have a minimum tendency to form deposits not only in the combustion chamber but also in the fuel system. The carburettor and intake manifold in particular are critical in this respect because there the fuel-air mixture is subjected to relatively high temperatures after the engine has been operated for some time and gums and resins are prone to form and interfere with the free flow of the fuel-air mixture and with the operation of the intake valves. This problem has been aggravated of late by the low profiles of the newer automobiles and the additional accessories in the engine compartment, such as air conditioning systems, which have considerably raised the normal engine compartment operating temperatures.

Still another important fuel characteristic is the extent of its tendency to develop static electrical charges during handling and the resulting likelihood that a spark discharge will occur. The extreme danger of this can largely be avoided if the fuel will conduct electricity to a substantial extent whereby the charges are dissipated to ground.

These problems of course are by no means all that the fuel manufacturer must overcome. However, it is evident that they are among the more important ones and a fuel improved in a number of these respects would be highly desirable.

In probably the last 20 to 30 years commercial gasoline has been composed of almost exclusively hydrocarbon components in so far as the energy-producing constituents are concerned. In the very early days of the use of spark ignition internal combustion engines alcohols were occasionally used as fuels; these were expensive and largely unsatisfactory in performance and were soon almost entirely abandoned in favour of hydrocarbon gasolines. During World War II branched alkyl ethers were proposed as high octane number components for aviation gasoline but they were not used on either a military or commercial scale.

It has now been found that certain concentrations of a particular class of ethers are surprisingly advantageous for practical use in hydrocarbon base fuels, especially for automotive engines, when used in conjunction with certain concentrations of a particular class of organic phosphorus compounds. In particular it has been found that when important concentration relationships are observed such ethers and such phosphorus compounds cooperate in a surprising way to provide a fuel

composition having greatly improved quality characteristics in the respects described above.

Thus according to the present invention a fuel composition comprises a hydrocarbon or a mixture of hydrocarbons boiling within the range of the boiling point of C_3 - C_4 hydrocarbons and 235°C . from 2% to 50% by volume of a dialkyl ether containing from 4 to 8 carbon atoms and having at least one alkyl group with a branched chain and from 0.001% to 0.1% by weight of a hydrocarbon-soluble organic phosphorus compound of the formula:



wherein:

X stands for an oxygen or sulphur atom;
R stands for a monovalent organic radical having from 1 to 10 carbon atoms and containing no atoms other than carbon hydrogen and halogen;

a is 0 or 1;

b and c are whole numbers from 0 to ~~6~~ inclusive;

and the sum of b + c is 3.

Ethers which are not of the kind defined above are not useful for the purposes of the present invention. For example, dialkyl ethers which do not contain at least one alkyl group with a branched chain have such low octane numbers that their incorporation into gasoline, for instance even in very small concentrations, could not be tolerated for use in modern high compression engines. Moreover, ethers containing less than 4 carbon atoms and more than 8 carbon atoms would not have suitable volatility to accomplish the purposes of the invention. It is preferred that the ethers of the invention contain 5 or 6 carbon atoms and that at least one of the two carbon atoms, attached to the single oxygen atom of the ether and preferably each of them is a secondary or a tertiary carbon atom. Within the preferred class of dialkyl ethers having 5 or 6 carbon atoms and at least one alkyl group with a branched chain, methyl tertiarybutyl ether, and especially diisopropyl ether are superior. Other suitable ethers within the scope of the invention include ethyl tertiarybutyl ether, isopropyl secondary butyl ether, isopropyl tertiarybutyl ether, methyl tertiaryamyl ether, ethyl isopropyl ether, methyl secondary butyl ether and methyl tertiaryhexyl ether.

An especially suitable ether component for the composition of the invention is a commercial diisopropyl ether product containing a minor amount of isopropyl alcohol which is obtained by the reaction of propylene with water in a sulphuric acid medium, for example in accordance with the processes disclosed in U.S. 2,055,720 or in U.S. 2,178,186. A typical product contains a high concentration of diisopropyl ether, a smaller but substantial concentration of isopropyl alcohol, small concentrations each of ethyl isopropyl ether, ethyl alcohol, C_6 to C_{12} propylene polymer, water and in some cases minute amounts of



3/

C₃ to C₄ hydrocarbons. The following are analyses of specific compositions which exemplify such suitable ether products:

		% by weight				
		A	B	C	D	E
5	Diisopropyl ether ..	97.6	98.1	85.9	89.1	85.3
	Isopropyl alcohol ..	1.1	1.0	4.7	7.7	12.2
10	Ethyl isopropyl ether ..	<0.1	<0.1	0.3	<0.1	0.1
	Ethyl alcohol ..	0.5	0.5	0.5	0.2	0.2
	C ₆ H ₁₂ ..	0.4	<0.1	1.2	2.2	1.1
	C ₉ H ₁₈ ..	0.2		3.0	0.6	0.2
15	C ₁₂ H ₂₄ ..			3.8	<0.1	0.1
	H ₂ O ..	<0.1	0.2	0.6	0.2	1.0

The organic phosphorus compound suitable for use in the composition of the invention must be hydrocarbon soluble. It may be a phosphine, phosphine oxide, phosphite, phosphonite, phosphinite, phosphate, phosphonate, phosphinate or a sulphur analogue thereof. The organic radical or radicals of the phosphorus compound may be an alkyl (acyclic or cyclic) or aryl group. They are preferably hydrocarbon radicals (that is radicals containing only carbon and hydrogen atoms) and especially cyclic hydrocarbon radicals. However, if desired, any radical may also contain a halogen atom, in which case the halogen atom is preferably chlorine or bromine, and especially chlorine. Of the cyclic radicals alkaryl groups are preferred. It is preferred that at least one and preferably all the radicals contain at least 4, and especially at least 6 carbon atoms. Particularly suitable are the trihydrocarbyl phosphates, trihydrocarbyl phosphites and trihydrocarbyl phosphines.

The following phosphorus compounds may be present in the composition of the invention: tricresyl phosphate, tributyl phosphate, tributyl phosphite, diphenyl cresyl phosphate, triphenyl phosphate, octyl diphenyl phosphate, triamyl thionophosphate, triphenyl phosphine, trimethyl phosphine oxide, tris(2-propyl)phosphite, bis(2-propyl) 2-propylphosphonate, trimethyl phosphate, trimethyl phosphite, phenyl dimethylphosphinate, propyl dicresyl thiophosphate, tris(3,3,5-trimethylcyclohexyl)phosphate, tris(2-chloropropyl)thionophosphate, diphenyl cresylphosphonite, dimethyl xylol phosphate, dimethyl cresyl phosphate, ethyl dimethylthiophosphinite, dimethyl phenyl phosphate and dimethyl phenylphosphonate.

It is critical for the purposes of the invention that a proper selection of concentrations of both the ether and phosphorus compound be made.

The concentration of the dialkylether must be at least 2% by volume and preferably at least 4% by volume. Ether concentrations of more than 50% by volume are not only usually unnecessary but would be deleterious in various respects. It is preferred that no more than 25%

and especially no more than 17% by volume of the ether be present in the fuel composition. Especially preferred ether concentrations are from about 6 to 15% by volume.

The phosphorus compound must be present at a concentration of at least 0.001% by weight and no more than 0.1% by weight. It is preferred that at least 0.01% by weight of the phosphorus compound be present. It is also preferred that no more than 0.06% by weight be present. Moreover, in addition to these weight limitations to the concentration of the phosphorus compound it is critical for the purposes of the invention that where a lead anti-knock agent such as a tetraalkyl lead, e.g. tetraethyl lead, is present, the concentration of the phosphorus compound is no less than 0.05 theory and no more than 0.6 theory. Preferred theory concentrations for the phosphorus compound are at least 0.2 theory and no more than 0.4 theory. In this connection it should be noted that one "theory" as the term is used herein referring to a phosphorus compound designates the amount of phosphorus compound stoichiometrically equivalent with the lead in the lead anti-knock agent present, i.e. so that all of the lead atoms and all of the phosphorus atoms are present in the same proportion as in the compound Pb₃(PO₄)₂. Thus in a given composition containing a lead anti-knock compound and a phosphorus compound, where T_P = theories of the phosphorus compound present, M_P = the number of gram mols of the phosphorus compound present, and A_L = the number of gram atoms of lead in the lead anti-detonant present:

$$T_P = \frac{(3/2)M_P}{A_L}$$

The base liquid of the fuel composition of the present invention may consist of gasoline which may be obtained by straight-run distillation, by thermally or catalytically cracking or by thermally or catalytically reforming. The base liquid may also be a product obtained by alkylation of lower molecular weight olefins and isoparaffins, for example of butylene and isobutane. The liquid which forms the base of the fuel composition of the invention must be a hydrocarbon or a mixture of hydrocarbons boiling in a broad range from the boiling points of C₃ to C₄ hydrocarbons to 235°C, preferably from 25°C to 220°C and especially from 35°C to 190°C.

Because abnormal combustion in modern high compression engines has become so complicated, it has been necessary to evaluate any given fuel proposed for commercial use on the basis of criterions which will ensure customer satisfaction with the fuel. An especially straightforward measurement of the adequacy of the fuel in these engines is the noise-limited power obtainable from an engine operated on the fuel in question. As explained above irregularities in combustion are evidenced

by noises quite different from those of normal combustion. It is extremely difficult, however, to distinguish between the different kinds of combustion irregularities and in the final analysis it really does not make much difference exactly how combustion is deviating from the normal—it is the fact that it is, which is important. The operator of an automobile is, of course, justified in caring only for maximum power and economy without encountering any noises symptomatic of inadequacy of the fuel. A simple and direct way of judging the quality of the fuel in respect to efficient combustion is therefore to operate the engine at a given speed under gradually increasing load and gradually increasing throttle opening until abnormal combustion noises are encountered. This is almost exactly how in practice the operator of an automobile evaluates the quality of the fuel he is using, for example, in climbing a hill the operator will gradually open the throttle as far as possible until a combustion noise is detected, at which time he will close the throttle a bit until the noise stops. With a high quality fuel no noise may be encountered at all even at wide open throttle; in this case the power extracted from the fuel is the maximum possible for this engine in its particular mechanical condition.

The benefits of the present invention are strikingly illustrated by this technique. A large number of gasoline blends have thus been evaluated in recent model automobiles having engines of 9.5 to 10.5 compression ratio. It was found that at 2500 rpm engine speed, for example, and using a gasoline having a road octane number of 98–100 and containing 2–3 cc TEL per 3.785 litres, the noise-limited power was, after equilibrium engine deposits had been formed, about 35–50 brake horsepower (BHP) at the rear wheels of the automobile. Adding enough diisopropyl ether or methyl tertiarybutyl ether to this gasoline to raise the road octane number by 1 to 2 numbers, for example 5 to 10% by volume, and again operating the engine from clean condition to equilibrium combustion deposits quite surprisingly did not increase the noise limited power obtained as compared with the base liquid. However, the addition of tricresyl phosphate, for example, to this base liquid without any ether, in a concentration of from 0.1 to 0.4 theory very substantially raised the noise limited power obtained in these tests. Tricresyl phosphate at 0.3 theory in particular raised the noise limited power of the base gasoline to the range of 75 to 80 BHP. It is possible that this benefit was because in the tests with the base liquid and the base plus ether the engine was limited, after equilibrium deposit had been built up, not by ordinary spark knock but by deposit phenomena. Now when both tricresyl phosphate and diisopropyl ether or methyl tertiarybutyl ether, were added to the gasoline, for example at the same

concentration of the ether again to raise the road octane number of the gasoline by one or two numbers, and at 0.3 theory of tricresyl phosphate (which of course does not in itself change the octane number of gasoline at all), it was found that noise limited power was raised to the range 85 to 90 BHP. Thus it can be seen that while the ether did no good at all by itself under these conditions, in the presence of phosphorus it had a substantial benefit over and above the benefits obtained from the phosphorus compound alone.

A most interesting aspect of the composition of the invention is that apparently the ether and the phosphorus compound co-operate to provide improved engine cleanliness and distribution of the high boiling constituents of the gasoline and relatively non-volatile additives among the cylinders. The phosphorus compounds in question have boiling points which are relatively high compared with the average of the gasoline as a whole; moreover, their viscosities are relatively high and in fact several of them are commercially used as plasticisers, for example tricresyl phosphate. On the other hand, the ether component is a better solvent for gums and other resinous deposits encountered in internal combustion engines than are the conventional hydrocarbon components, especially the non-aromatic ones, of the gasoline; this is probably because of the oxygenated character of both the gums and ethers. The mechanism leading to improved engine cleanliness seems to be that when an engine operated with the present composition is started the intake manifold is usually relatively cool and a substantial quantity of the ethers, even though they are relatively volatile, appear in a liquid phase on the walls of the intake manifold. The phosphorus compound softens or plasticises any existing deposit making it easier for the ether to pull the deposits into the liquid whereby they are carried through to the combustion chamber where they are burned. Subsequently-formed deposits which may occur during an extended operation of the engine at normal operating temperatures are then taken into solution during the next warm-up cycle of the engine.

The improved distribution effect of the combination of ether and phosphorus compound is apparently brought about by the increased tendency of the liquid phase of the high boiling constituents of the gasoline to creep along the walls of the intake manifold toward the combustion chambers. As the fuel-air mixture leaves the carburettor and enters the intake manifold it is partly in vapour form and partly in the form of dispersed liquid droplets. A substantial proportion of these liquid droplets collect as a liquid phase on the walls of the intake manifold. As this liquid phase moves toward the combustion chambers the low-boiling constituents therein continue to evaporate. The relatively non-volatile

phosphorus compound of the composition of the invention has a higher surface tension than the major proportion of the gasoline, while the relatively volatile ether has a lower surface tension than the major proportion of the gasoline; there is therefore a positive surface tension gradient in the direction from the carburettor to the combustion chambers. It has been found that under such circumstances a liquid phase will have a tendency to creep against the force of gravity. The extent of the forces pulling the liquid film against gravity are directly proportional to the difference in the surface tensions of the components evaporating from the liquid film and the high boiling constituents left behind. The ethers of the present class have generally much lower surface tensions than gasoline hydrocarbons. For example, the surface tension of diisopropyl ether at 25°C is 17.3 dynes/cm (Vogel, A.I., J.Chem.Soc., Part I, 616 (1948) as compared to about 26 dynes/cm for gasoline hydrocarbons. Thus, the addition of both the ether and the phosphorus compound to gasoline hydrocarbons very substantially increases the surface tension gradient of the liquid along the walls of the intake manifold and thus increases its mobility, resulting in better distribution of the high boiling constituents of the gasoline and low volatility additives among the cylinders.

The gasoline compositions of the invention have still another attribute of importance. This is their surprisingly low tendency to develop electrostatic charges. It has been discovered that the ethers and phosphorus compounds of the present gasoline composition co-operate in an unexpected fashion to increase the electrical conductivity of gasoline. For example a gasoline was measured and found to have an electrical conductivity of 17×10^{-14} ohm⁻¹ cm⁻¹. The addition of 3 cc of tetraethyl lead per 3.785 litres to the gasoline made very little difference; the conductivity was 15×10^{-14} ohm⁻¹ cm⁻¹. Adding 0.3 grams of tricresyl phosphate per 3.785 litres to the gasoline also made little difference; the conductivity was 19×10^{-14} ohm⁻¹ cm⁻¹. The addition of 10% by volume of diisopropyl ether to the gasoline increased the conductivity to some extent, i.e. to 27×10^{-14} ohm⁻¹ cm⁻¹. However, adding these same concentrations of tricresyl phosphate and diisopropyl ether together to the gasoline more than doubled the electrical conductivity, i.e. raised it to 37×10^{-14} ohm⁻¹ cm⁻¹, and the addition of these same concentrations of tricresyl phosphate, diisopropyl ether and tetraethyl lead to the gasoline about doubled its conductivity, i.e. raised it to 33×10^{-14} ohm⁻¹ cm⁻¹.

Besides the ether and phosphorus compound the composition of the invention preferably contains an anti-knock concentration of a lead anti-detonant, e.g. a tetra-alkyl lead compound for example tetraethyl lead. The advantages of the presence of the ether and phosphorus

compound in a number of the important respects already discussed have been found to occur in the presence of such a lead anti-knock agent. The concentration of the lead anti-knock agents is preferably at least 0.5 cc per 3.785 litres and up to 6 cc per 3.785 litres, more especially at least 1 cc per 3.785 litres and no more than 3 cc per 3.785 litres. When a lead anti-knock agent is used a halohydrocarbon scavenger such as ethylene dibromide or a mixture of ethylene dibromide and ethylene dichloride is preferably added in conjunction therewith, especially in an amount of from 1.0 to 1.5 or 1.6 theories, 1.0 theory being the amount necessary to provide two atoms of halogen per atom of lead in the lead anti-knock agent present. Also useful in the composition of the invention are other anti-knock agents, for example iron carbonyl, dicyclopentadienyl iron, xylylene, N-methylaniline and the organomanganese compounds, especially methylcyclopentadienyl manganese tricarbonyl, or bis(cyclopentadienyl) manganese. Such compounds are suitably used either as the only anti-knock agent or preferably as a supplemental anti-knock agent with for example tetraethyl lead.

Other additives suitably used if desired in the composition of the invention include the various anti-icing agents, for example N-C₁₂₋₁₈-alkylpropylenediamine and dimethylformamide; combustion chamber deposit modifiers, e.g. glycol esters of boric acid for example isopropyl 2-methyl-2,4-pentanediol borate, 2-methyl-2,4-pentanediol monoacid borate, bis-(1,1,3-trimethyl-trimethyleneoxy)-boric oxide; anti-oxidants such as N,N'-disecundarybutylphenylenediamine, 2,6-ditertiarybutyl-4-methyl-phenol, 4,4'-methylene bis(2,6-ditertiary-butylphenol); corrosion inhibitors, for example polymerised linoleic acids and N,C-disubstituted imidazolines; metal deactivators for example N,N'-disalicylal-1,2-propanediamine; dyes, and silicone oils.

Besides the gasoline compositions described above, an especially suitable example of the composition of the invention is the following:

1. Petroleum gasoline hydrocarbons ..	90% by volume	
Diisopropyl ether (the commercial product obtained by reaction of water and propylene described and identified above as "D") ..	10% by volume	120
Tetraethyl lead ..	2.8 cc/3.785 litres	
Ethylene dibromide ..	0.5 theory	
Ethylene dichloride ..	1.0 theory	
Tricresyl phosphate ..	0.3 theory (i.e. 0.38% by weight)	125
N-C ₁₂ -alkyl-1,3-propanediamine ..	(0.003% by weight)	130

N,N'-disecundarybutyl-phenylenediamine .. (0.0005% by weight)

This composition has an ASTM Research Method octane number of 102.0 (Wiese scale, or isooctane + 0.16 cc TEL/3.785 litres), an ASTM Motor Method octane number of 92.5 and an ASTM distillation of from 38°C to 204°C.

10 Other suitable examples of the composition of the invention, which may also contain various other minor components as described above, include:

15 2. Petroleum gasoline hydrocarbons .. 85% by volume
Methyl tertiarybutyl ether .. 15% by volume
Tetraethyl lead .. 3 cc/3.785 litres
Tributyl phosphate .. 0.2 theory

20 3. Petroleum gasoline hydrocarbons .. 80% by volume
Diisopropyl ether .. 20% by volume
Tricresyl phosphate .. 0.02% by weight

25 4. Petroleum gasoline hydrocarbons .. 88% by volume
Diisopropyl ether .. 12% by volume
Tetraethyl lead .. 2 cc/3.785 litres
Octyl diphenyl phosphate .. 0.2 theory

30 5. Petroleum gasoline hydrocarbons .. 95% by volume
Isopropyl tertiarybutyl ether .. 5% by volume
Tetraethyl lead .. 2.5 cc/3.785 litres

35 Dimethyl xylyl phosphate .. 0.15 theory

40 6. Petroleum gasoline hydrocarbons .. 90% by volume
Diisopropyl ether .. 10% by volume
Tetraethyl lead .. 2.5 cc/3.785 litres

Tributyl phosphine .. 0.10 theory

45 7. Petroleum gasoline hydrocarbons .. 91% by volume
Methyl tertiarybutyl ether .. 9% by volume
Tetraethyl lead .. 2.8 cc/3.785 litres

50 Tris(2-chloropropyl)thiophosphate .. 0.1 theory

55 8. Petroleum gasoline hydrocarbons .. 85% by volume
Ethyl tertiarybutyl ether .. 15% by volume
Tetraethyl lead .. 3.0 cc/3.785 litres

Methylcyclopentadienyl manganese tricarbonyl .. 0.1 gram of manganese/3.785 litres

60 Tricresyl phosphate .. 0.3 theory

65 9. Petroleum gasoline hydrocarbons .. 96% by volume
Diisopropyl ether .. 4% by volume
Tetraethyl lead .. 3 cc/3.785 litres

Tricresyl phosphate .. 0.4 theory
10. Petroleum gasoline hydrocarbons .. 92% by volume
Isopropyl tertiaryamyl ether .. 8% by volume 70
Tetraethyl lead .. 2.4 cc/3.785 litres

Diphenyl cresyl phosphate .. 0.12 theory
11. Petroleum gasoline hydrocarbons .. 85% by volume 75
Diisopropyl ether .. 15% by volume
Tetraethyl lead .. 3.0 cc/3.785 litres

Tris(2-propyl)phosphite .. 0.2 theory 80
12. Petroleum gasoline hydrocarbons .. 88% by volume
Diisopropyl ether .. 12% by volume
Tetraethyl lead .. 2.8 cc/3.785 litres 85

Tris(2-propyl)phosphite .. 0.1 theory
Tricresyl phosphate .. 0.1 theory
13. Petroleum gasoline hydrocarbons .. 85% by volume 90
Methyl tertiarybutyl ether .. 15% by volume
Tetraethyl lead .. 2.5 cc/3.785 litres

Tricresyl phosphate .. 0.3 theory 95
14. Petroleum gasoline hydrocarbons .. 75% by volume
Diisopropyl ether .. 25% by volume
Tetraethyl lead .. 2.5 cc/3.785 litres

Dimethyl cresyl phosphate .. 0.08 theory 100
Dimethyl xylyl phosphate .. 0.08 theory

15. Petroleum gasoline hydrocarbons .. 93% by volume 105
Diisopropyl ether .. 7% by volume
Tetraethyl lead .. 2.7 cc/3.785 litres

Tricresyl phosphite .. 0.3 theory 110
WHAT WE CLAIM IS:—

1. A fuel composition comprising a hydrocarbon or a mixture of hydrocarbons boiling within the range of the boiling point of C_3-C_4 hydrocarbons and 235°C, from 2% to 50% by volume of a dialkyl ether containing from 4 to 8 carbon atoms and having at least one alkyl group with a branched chain and from 0.001% to 0.1% by weight of a hydrocarbon-soluble organic phosphorus compound of the formula:
 $P(X)_a(XR)_b(R)_c$ 120

wherein:

X stands for an oxygen or sulphur atom;
R stands for a monovalent organic radical having from 1 to 10 carbon atoms and containing no atoms other than carbon, hydrogen and halogen; 125

a is 0 or 1;

b and c are whole numbers from 0 to 3 inclusive;

and the sum of b + c is 3. 130

N,N'-disecundarybutyl-phenylenediamine .. (0.0005% by weight)

5 This composition has an ASTM Research Method octane number of 102.0 (Wiese scale, or isooctane + 0.16 cc TEL/3.785 litres), an ASTM Motor Method octane number of 92.5 and an ASTM distillation of from 38°C to 204°C.

10 Other suitable examples of the composition of the invention, which may also contain various other minor components as described above, include:

15 2. Petroleum gasoline hydrocarbons .. 85% by volume
Methyl tertiarybutyl ether .. 15% by volume
Tetraethyl lead .. 3 cc/3.785 litres
Tributyl phosphate .. 0.2 theory

20 3. Petroleum gasoline hydrocarbons .. 80% by volume
Diisopropyl ether .. 20% by volume
Tricresyl phosphate .. 0.02% by weight

25 4. Petroleum gasoline hydrocarbons .. 88% by volume
Diisopropyl ether .. 12% by volume
Tetraethyl lead .. 2 cc/3.785 litres
Octyl diphenyl phosphate .. 0.2 theory

30 5. Petroleum gasoline hydrocarbons .. 95% by volume
Isopropyl tertiarybutyl ether .. 5% by volume
Tetraethyl lead .. 2.5 cc/3.785 litres

35 Dimethyl xylyl phosphate .. 0.15 theory

40 6. Petroleum gasoline hydrocarbons .. 90% by volume
Diisopropyl ether .. 10% by volume
Tetraethyl lead .. 2.5 cc/3.785 litres

45 Tributyl phosphine .. 0.10 theory
7. Petroleum gasoline hydrocarbons .. 91% by volume
Methyl tertiarybutyl ether .. 9% by volume
Tetraethyl lead .. 2.8 cc/3.785 litres

50 Tris(2-chloropropyl)thionophosphate .. 0.1 theory

55 8. Petroleum gasoline hydrocarbons .. 85% by volume
Ethyl tertiarybutyl ether .. 15% by volume
Tetraethyl lead .. 3.0 cc/3.785 litres

Methylcyclopentadienyl manganese tricarbonyl .. 0.1 gram of manganese/3.785 litres

60 Tricresyl phosphate .. 0.3 theory

9. Petroleum gasoline hydrocarbons .. 96% by volume
Diisopropyl ether .. 4% by volume
65 Tetraethyl lead .. 3 cc/3.785 litres

Tricresyl phosphate .. 0.4 theory
10. Petroleum gasoline hydrocarbons .. 92% by volume
Isopropyl tertiaryamyl ether .. 8% by volume
Tetraethyl lead .. 2.4 cc/3.785 litres

Diphenyl cresyl phosphate .. 0.12 theory
75 11. Petroleum gasoline hydrocarbons .. 85% by volume
Diisopropyl ether .. 15% by volume
Tetraethyl lead .. 3.0 cc/3.785 litres

Tris(2-propyl)phosphite .. 0.2 theory
80 12. Petroleum gasoline hydrocarbons .. 88% by volume
Diisopropyl ether .. 12% by volume
Tetraethyl lead .. 2.8 cc/3.785 litres

85 Tris(2-propyl)phosphite .. 0.1 theory
Tricresyl phosphate .. 0.1 theory
13. Petroleum gasoline hydrocarbons .. 85% by volume
Methyl tertiarybutyl ether .. 15% by volume
Tetraethyl lead .. 2.5 cc/3.785 litres

Tricresyl phosphate .. 0.3 theory
95 14. Petroleum gasoline hydrocarbons .. 75% by volume
Diisopropyl ether .. 25% by volume
Tetraethyl lead .. 2.5 cc/3.785 litres

100 Dimethyl cresyl phosphate .. 0.08 theory
Dimethyl xylyl phosphate .. 0.08 theory

15. Petroleum gasoline hydrocarbons .. 93% by volume
Diisopropyl ether .. 7% by volume
Tetraethyl lead .. 2.7 cc/3.785 litres

Tricresyl phosphite .. 0.3 theory
110 WHAT WE CLAIM IS:—

1. A fuel composition comprising a hydrocarbon or a mixture of hydrocarbons boiling within the range of the boiling point of C₃-C₄ hydrocarbons and 235°C, from 2% to 50% by volume of a dialkyl ether containing from 4 to 8 carbon atoms and having at least one alkyl group with a branched chain and from 0.001% to 0.1% by weight of a hydrocarbon-soluble organic phosphorus compound of the formula:



wherein:

X stands for an oxygen or sulphur atom;
R stands for a monovalent organic radical having from 1 to 10 carbon atoms and containing no atoms other than carbon, hydrogen and halogen;
a is 0 or 1;
b and c are whole numbers from 0 to 3 inclusive;
and the sum of b + c is 3.
120
125
130



2. A fuel composition as claimed in claim 1, wherein the dialkyl ether contains 5 or 6 carbon atoms.
3. A fuel composition as claimed in claim 1 or 2, wherein of the two carbon atoms which are linked to the oxygen atom in the dialkyl ether, at least one and preferably each is a secondary or a tertiary carbon atom.
4. A fuel composition as claimed in claim 1 or 2, wherein the dialkyl ether is methyl tertiary-butyl ether.
5. A fuel composition as claimed in any one of claims 1-3, wherein the dialkyl ether is diisopropyl ether.
6. A fuel composition as claimed in any one of the preceding claims, wherein the dialkyl ether is present in a proportion of from 4% to 25% by volume.
7. A fuel composition as claimed in any one of the preceding claims, wherein the dialkyl ether is present in a proportion of from 6% to 15% by volume.
8. A fuel composition as claimed in any one of the preceding claims, wherein the phosphorus compound contains hydrocarbon radicals.
9. A fuel composition as claimed in claim 8, wherein the phosphorus compound contains cyclic hydrocarbon radicals.
10. A fuel composition as claimed in claim 9, wherein the cyclic hydrocarbon radicals are alkaryl groups.
11. A fuel composition as claimed in claim 1, wherein the monovalent radicals in the phosphorus compounds contain at least 4 carbon atoms.
12. A fuel composition as claimed in claim 11, wherein the monovalent radicals in the phosphorus compound contain at least 6 carbon atoms.
13. A fuel composition as claimed in any one of claims 1 and 8-12, wherein the phosphorus compound is a tri hydrocarbyl phosphate.
14. A fuel composition as claimed in claim 13, wherein the phosphorus compound is tricresyl phosphate.
15. A fuel composition as claimed in any one of claims 1 and 8-12, wherein the phosphorus compound is a trihydrocarbyl phosphite.
16. A fuel composition as claimed in any one of claims 1 and 8-12, wherein the phosphorus compound is a trihydrocarbyl phosphine.
17. A fuel composition as claimed in any one of claims 1 and 8-16, wherein the phosphorus compound is present in a proportion of from 0.01% to 0.06% by weight.
18. A fuel composition as claimed in any one of claims 1 and 8-16, containing a lead anti-knock agent in which the proportion of the phosphorus compound is 0.05-0.6 theory.
19. A fuel composition as claimed in claim 18, wherein the proportion of the phosphorus compound is 0.2-0.4 theory.
20. A fuel composition as claimed in any one of the preceding claims, wherein the base liquid is a hydrocarbon or a mixture of hydrocarbons boiling within a range from 25°C to 220°C.
21. A fuel composition as claimed in claim 20, wherein the base liquid is a hydrocarbon or a mixture of hydrocarbons boiling within a range from 35°C to 190°C.
22. A fuel composition as claimed in any one of claims 1, 20 and 21, wherein the base liquid is a gasoline.
23. A fuel composition as claimed in claim 22, wherein the base liquid is a straight-run gasoline.
24. A fuel composition as claimed in claim 22, wherein the base liquid is a thermally or catalytically cracked gasoline.
25. A fuel composition as claimed in claim 22, wherein the base liquid is a thermally or catalytically reformed gasoline.
26. Fuel compositions substantially as hereinbefore described.
27. Fuel compositions as hereinbefore described with reference to the foregoing Examples.
- DOWNES & ROBBINS,
Chartered Patent Agents,
St. Helen's Court, Great St. Helen's,
London, E.C.3.
Agents for the Applicants.

Bournemouth: Printed for Her Majesty's Stationery Office, by Richmond Hill Printing Works Ltd.—1960.
Published at The Patent Office, 25, Southampton Buildings, London, W.C.2, from which copies may be obtained.

