Patented July 27, 1948 2,445,778

UNITED STATES PATENT OFFICE

2,445,778

FUELS FOR INTERNAL-COMBUSTION ENGINES

William J. Hale, Midland, Mich.

No Drawing. Application June 27, 1945, Serial No. 601,915

6 Claims. (Cl. 44—53)

1

This invention relates to improved fuels for internal combustion engines, more particularly to an improved fuel containing heavy metallic complexes of porphyrins.

The present application is a continuation-in-part of prior application, Serial No. 559,131, filed October 17, 1944.

Porphines comprise that class of ring compounds made up of four pyrrole nuclei linked at their α-carbon positions through one of the four methine (—CH=) bridges. The remaining eight hydrogen atoms at the β-carbon positions in these pyrrole rings are numbered clockwise and may be substituted by alkyl, aryl and other groups, and when one or more are so substituted we arrive at the type of compound known as porphyrin.

Of paramount importance here are the four isomeric forms of tetramethyl tetraethyl porphine known as etioporphyrins, recently synthesized, and of which one isomer, in which the methyl groups occupy positions 1, 3, 5 and 8, constitutes the essential base of both chlorophyll and hemin, thus establishing the close interrelationship of same.

As pointed out in the prior application referred to this entire class of compounds possesses the characteristic of taking a metal atom into its molecular center and holding the same in direct union with the several nitrogen atoms of the four pyrrole nuclei thus forming a metallic-complex porphyrin and now known generally as a phyllin. Thus, etiophyllin is the magnesium complex of etioporphyrin.

When we reduce partially the pyrrole ring IV of basic porphine we arrive at Chlorin; and if we then establish a 5-numbered carbocyclic ring between carbon-6 position and the γ-methine group we arrive at Phorbin. It is on the structure of phorbin that the well-known chlorophyll is established; chlorophyll-a is the phytyl ester of 9-oxo-10-methylcarboxy-1, 3, 5, 8-tetramethyl-2-vinyl 4-ethyl-magnesium-phorbin-7-propionic acid while chlorophyll-b is a modification thereof in which 3-methyl becomes 3-formyl.

In nature, chlorophyll-a plays the role of reducing agent for carbonic acid wherein the resulting chlorophyll-b becomes an oxidizing agent. The accompanying carotenes within the green leaf serve as acceptors for the oxygen given up by chlorophyll-b in its reformation into chlorophyll-a, they themselves becomes xanthophylls; and numerous enzymes present serve to reconvert xanthophylls into carotenes to enter again the oxidation-reduction cycle.

2

The marked oxidation action of chlorophyll in the presence of air is well-known; its directive action being dependent upon the presence of acceptors. In the copending application referred to it was disclosed that chlorophyll would materially aid in the combustion of simple hydrocarbons, as is gasoline, when supplied to same in the ordinary internal combustion engine; and so also other porphyrin compounds as, e. g., hemin may be made to serve in like capacity.

This definite beneficial function of chlorophyll as an oxidant in the combustion of hydrocarbons was evidenced in the analysis of exhaust gases issuing from combustion chamber. Whereas, under ordinary circumstances with high octane gasoline, and excess air, never less than a content of 4% carbon monoxide is detectable in these exhaust gases, the introduction to same quality of gasoline of only $\frac{1}{10}$ of 1% its weight of chlorophyll insured a reduction by 50% in the carbon monoxide content in the exhaust. This same degree of reduction, by 50% in carbon monoxide content in exhaust gases, may be secured when 10% by volume of alcohol is admixed with gasoline before entering the motor (Brown & Christensen, Ind. Eng. Chem. 28, 650 (1936)). The association, therefore, of these two oxidation factors, —10% alcohol content in gasoline and $\frac{1}{10}$ of 1% by weight of chlorophyll contributed, as may be expected, to a drop of over 70% in carbon monoxide content under that usually present when neither alcohol nor chlorophyll is present; all of which has been set forth in the patent application cited.

The mechanism of this oxidative action of chlorophyll is perfectly understandable and accords with the cycle above described. There is accumulating evidence, however, that the aldehydic group in carbon-3 position in chlorophyll-b is likewise capable under pressure of affixing to its oxygen still additional oxygen and thus is made to effect more extensive oxidation among the surrounding organic molecules. Furthermore, it is to be observed that much of the oxidative power of phorbins lies in the vinyl group; so also it has been shown by Fischer & Riedmair (Ann. d. Chem. 506, 107 (1933)) that the hydrogen atom at carbon-10 position is exceptionally active—hence greatest significance must be attached generally to the phorbin type of structure as highly conducive to oxidative processes. The tendency for such structures to take up molecular oxygen (molecule per molecule) to undergo what is termed allomerization corroborates

further the oxidative properties displayed by chlorophyll.

But chlorophyll usually supplied, and known to consist of about 3 parts chlorophyll-*a* to 1 part chlorophyll-*b*, is accompanied by a heterogeneous mixture of plant extractables. As extracted directly from verdure by means of low boiling hydrocarbons the dried extract from 2000 lbs. (900,000 grams) of air dried alfalfa usually analyzes for 3500 grams of chlorophyll-*a*+*b* ($\frac{4}{10}$ of 1%) and 600 grams of carotenoids ($\frac{7}{100}$ of 1%) and 22,000 grams of fats, waxes and resins (2.4%). Of the total dry extract scarcely more than 12% is represented by the chlorophylls. The employment of such crude material is not to be recommended for use in the internal combustion engine, for the reason that gumming of spark plugs and valves may result.

Recourse to isolation of the chlorophyll content of these crude extracts introduces a complexity of possibilities. Nevertheless, a fairly pure and crystalline chlorophyll was secured and tested as set forth in the prior cross referenced application. The results have been verified time after time. The commercial producers of this chlorophyll have generally chosen to remove the chlorophyll in an alcohol-water solvent but deprived of its magnesium, i. e., in what is known as pheophytin-*a* and pheophytin-*b*; then later they have removed the phytyl group thus leading to pheophorbide-*a* and pheophorbide-*b*; anyone of which, when introduced into gasoline for internal combustion engine served well to catalyze fuller oxidation of hydrocarbon.

It was found that when other metallo magnesium chlorophyll complexes were tested a decided improvement in the direction of oxidation was observed. Furthermore, a marked increase in anti-detonating properties among certain of the newly treated gasolines was detected. Notably here was the excellent result attained when the water soluble metallo-iron complex of chlorophyll was employed. In that the removal of the phytyl group from chlorophyll is described as leading to a chlorophyllide and the removal of both phytyl and methyl (from carbomethoxyl at carbon-10 position) is described as leading to a chlorophyllin, both of which are very soluble in alcohol as well as in water, these forms of chlorophyll may well be described as "water soluble." The metallo-iron complex, as above described, is therefore to be looked upon as iron chlorophyllin, and usually here also in form of a sodium salt though this latter is not to be recommended.

When iron chlorophyllin, free from gums and resins, was introduced into gasoline to the extent of $\frac{1}{10}$ of 1% by weight and the gasoline with excess air subjected to combustion in an internal combustion engine and analysis made of the exhaust gases there was found scarcely ½ of 1% of noxious carbon monoxide. The catalytic effect of the iron chlorophyllin on extent of combustion without knock proved phenomenal. The above experiment was repeated substituting a 10% alcohol-gasoline blend for the gasoline itself. Analysis of the exhaust gases from this fuel showed scarcely more than a trace of carbon monoxide. Careful repetition of these experiments but returning to the use of the former magnesium chlorophyllin was never made to approach the results obtained with the iron complex.

Evidently the mechanism of this improved action is not unlike the action of lead tetraethyl in its decomposition at time of combustion of "leaded" or "ethyl gasoline." The finely divided atomic lead liberated in the combustion cylinders serves the purpose of control in spread of flame, with a resulting smooth and even combustion. Iron derived from iron carbonyl is well-known to function similarly. So also cobalt, chromium, manganese, palladium, gold, tellurium and other metals.

The usual content of metallic lead in ordinary "ethyl gasoline," where 3 cc. of ethyl fluid is added per gallon, amounts to about 1.89 grams per gallon. With $\frac{1}{10}$ of 1% content of iron chlorophyllin introduced into a gallon (6.25 lbs.) of gasoline only 0.25 gram of iron is present per gallon. Hence, in comparison of atomic iron with atomic lead, with full consideration of their respective atomic weights, it will be observed that there is about ½ the number of iron atoms as compared with lead entering by way of ordinary "ethyl gasoline"; and a very favorable comparison in efficiency. Indeed, the reduction in concentration of iron chlorophyllin to $\frac{1}{100}$ of 1% the weight of gasoline is found to be quite satisfactory.

It is in this latter connection that the effect of iron chlorophyllin is to be found to be enhanced by the addition of alcohol. When a 10% alcohol-gasoline blend is employed the introduction of $\frac{1}{100}$ of 1% content of iron chlorophyllin in accompanied by most highly satisfactory results; this latter accords with the observation of Willstaetter and Stoll (Ann. 382,129) (1911)) on increase in chlorophyll oxidation through presence of alcohol.

Over and above all considerations based on the vaporization of finely divided metal in the combustion cylinders of the internal combustion engine whereby to serve as anti-detonator, we must consider also the ways and means of eliminating this metal so soon as spent; otherwise the spark plug electrodes and valves will accumulate metallic deposits. In the case of ethyl gasoline there is made to be present a sufficient amount of ethylene dibromide such that in the process of combustion practically all of the lead is removed in the exhaust vapors in the form of difficultly hydrolyzable lead dibromide. In the case of iron chlorophyllin there is no attending reactant capable of combining with and removing the spent iron.

On the other hand, with iron chlorophyllin, there is a much smaller weight of metal to be removed than when leaded gasoline is used; especially when operating on a content of as little as 1/100 of 1% iron chlorophyllin per gallon of fuel, and still much less when operating on 1/1000 of 1% iron chlorophyllin per gallon of fuel, as is known to serve well. But the most striking feature in connection with the use of iron chlorophyllin is the tendency for the spent iron to deposit upon the walls of combustion cylinder whereby to exert further its anti-detonating power until dissolved away in the form of iron carbonyl by agency of free carbon monoxide in the combustion zone, and then finally the discharge of the spent iron in volatile form through the exhaust. This mechanism, therefore, accounts for the almost total elimination of free carbon monoxide as such when iron chlorophyll and alcohol were present in hydrocarbon fuel. This general result was not discovered heretofore simply by reason of the use of magnesium chlorophyll, a compound that generates magnesium only to enter into its oxide without any capability of forming a volatile carbonyl, a characteristic of all of the electropositive elements.

Structurally there is not so wide a divergence between lead tetraethyl and iron or other metal-chlorophyllins. In the latter there are four nitrogen atoms attached to the metal complex with eight or more ethyl groups, or congeners, leading out from the nitrogen atoms but at the same time linked in pairs such as to form aromatic carbon-nitrogen nuclei fully substituted, a structure that may explain the favorable performance of dimethyl aniline in anti-detonating power. It is thus clear that the structure of metallo chlorophyllins offers the double opportunity of generating free metal in the atomic state in the combustion chamber and supplying anti-detonative carbon-nitrogen ring nuclei.

This invention, therefore, comprehends the utilization for adjuvants to hydrocarbon fuels of metals that may readily form carbonyls at higher temperatures and yet be capable of entering into metallo-complexes with porphyrins, chiefly those of the phorbin and hemin series; such metals may be described as heavy metals or metals equal to and above iron in atomic weight and specific gravity. Among the metals introducible into porphyrins in acid solution are iron, cobalt, nickel, manganese, chromium, molybdenum, tungsten, copper, silver, gold and zinc; in weakly alkaline solution (as in pyridine) are mercury, thallium, lead and tin; and in strongly alkaline solution are magnesium, lithium, sodium, potassium, rubidium and caesium. But of these metals only those that form volatile carbonyls can be expected to function in the direction desired. Though all of the metals of the Eighth Group of the Periodic System can form carbonyls, only iron, cobalt and nickel are serviceable here; of the seventh group of the periodic system, manganese alone is serviceable; of the sixth group of the periodic system chromium, molybdenum and tungsten are found to be effective to some extent; and of the first group copper, silver and gold are likewise effective. Though carbonyls of copper, silver, gold, chromium and manganese are not stable there is evidence of their formation incipiently.

In the newly introduced "Vita meter," or apparatus for supplying automatically through the carburetor to internal combustion engine a supplementary fuel composed of alcohol and water (usually in proportions of 50 to 50) and at times when the load on the motor calls for increased power, conditions obtain for which this type of improved fuel is eminently suited. In the first place, the Vita meter employs both alcohol and water and hence is the ideal solvent for the alcohol-water soluble metalloporphyrins; in the second place, the concentration of the metalloporphyrins in the aqueous alcohol can be stepped up at will such as to attain highest efficiency in the mixed fuels entering the carburetor. In general, the supplementary fuel to be supplied through the Vita meter need contain little more than $\frac{1}{10}$ of 1% by weight of metallo-porphyrins, such as iron or cobalt chlorophyllin, whereupon the fuel in combustion cylinders will carry a concentration of $\frac{1}{100}$ of 1% of the catalyst or less. However, the concentration of metallo-porphyrin may be increased in the supplementary fuel to as high as 1–3% by weight thereof and even higher with full assurance that a corresponding greater concentration of catalyst in combustion cylinders is attainable. If higher concentrations of the metallo-porphyrin are employed it is desirable to associate therewith some organic chemical carrying a halogen or other specific group capable of

combining with the metal portion of metallo-porphyrin such that the resulting compound may be discharged in the exhaust gases.

It has been established that water alone in the Vita-meter and entering the carburetor for admixture with the hydrocarbon fuel, insures improved performance, just as is evidenced in the driving of a motor or a moist day; but the results obtainable with admixture of alcohol and water far outstrip the performance of any other supplementary fuel. As described herein, the use of a metallo-porphyrin as a catalyst of great solubility therein adds materially to oxidative effect already inherent in the alcohol of such supplemental fuel and in conjunction with the alcohol, is conducive to high anti-detonative activity even of low grade gasolines.

The solution of iron chlorophyllin and similar compounds in alcohol-water presents an attractive green color, and remains unaffected by light over long periods if the destrictive red rays are filtered out (Dangeard (Compt. rend. 151, 1386 1910)). To this end green glass bottles (transmitting light of the same wave length as the chlorophyll compound) serve admirably. But still further the addition of oxygen acceptors is highly to be recommended, especially where alcohol is present. The best acceptors here are, of course, those that accompany chlorophyll in nature, namely, the carotenes. If further stability is desired a trace of isoamylamine has proved efficient. In all cases the alcohol or water or both should be freed of dissolved oxygen before use in compounding the metallo-porphyrin solutions.

It will be appreciated that the beneficially functioning compounds disclosed herein may be made available ultimately in the combustion chamber in a number of ways; they may be blended directly with the gasoline or, as described, may be dissolved in a suitable solvent, such as alcohol or alcohol water mixtures to be added continuously or intermittently to the stream of hydrocarbon fuels fed to the motor.

While preferred modifications of the invention have been described it is to be understood that these are given to explain the broad concept of the invention which involves the improvement performance of hydrocarbon fuels by inducing more complete oxidation of such fuels and reducing detonation by the employment of the described type of compounds.

I claim:

1. A liquid hydrocarbon fuel containing a heavy metallo-chlorophyllin, the metal component of which is chosen from the group consisting of iron, cobalt, nickel, manganese, chromium, molybdenum, tungsten and copper, which is substantially free from resins and waxes and in an amount sufficient to be effective as an antioxidant.

2. A liquid hydrocarbon fuel containing from $\frac{1}{100}$ to 3% of a heavy metallo-chlorophyllin, the metal component of which is chosen from the group consisting of iron, cobalt, nickel, manganese, chromium, molybdenum, tungsten and copper, which is substantially free from resins and waxes.

3. A liquid hydrocarbon fuel containing from $\frac{1}{10}$ of 1% to 1% of a heavy metallo-chlorophyllin, the metal component of which is chosen from the group consisting of iron, cobalt, nickel, manganese, chromium, molybdenum, tungsten and copper, which is substantially free from resins and waxes.

4. An alcohol-water fuel containing a heavy metallo-chlorophyllin, the metal component of which is chosen from the group consisting of iron, cobalt, nickel, manganese, chromium, molybdenum, tungsten and copper, which is substantially free from resins and waxes and in an amount sufficient to be effective as an antioxidant.

5. An alcohol-water fuel containing as an oxidant an anti-detonator from $\frac{1}{10}$ of 1% to 3% by weight of a resin-free heavy metallo-chlorophyllin, the metal component of which is chosen from the group consisting of iron, cobalt, nickel, manganese, chromium, molybdenum, tungsten and copper, which is substantially free from resins and waxes.

6. An alcohol-water fuel containing as an oxidant an anti-detonator from $\frac{1}{10}$ of 1% to 1% by

weight of a resin-free heavy metallo-chlorophyllin, the metal component of which is chosen from the group consisting of iron, cobalt, nickel, manganese, chromium, molybdenum, tungsten and copper, which is substantially free from resins and waxes.

WILLIAM J. HALE.

REFERENCES CITED

The following references are of record in the file of this patent:

FOREIGN PATENTS

Number	Country	Date
518,958	Great Britain	Mar. 12, 1940

OTHER REFERENCES

Chemical abstracts, vol. 27 (1933), page 201.