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FUEL FOR INTERNAL COMBUSTION ENGINES

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This invention relates to the operation of internal combustion engines and fuel therefor and specifically to the operation of engines using a fuel comprising a hydrocarbon such as gasoline, which normally produces a knock when used in high compression engines, the invention being concerned with the elimination of the knock.

The alkyl and aryl derivatives of various elements, both metallic and non-metallic, have been found useful in preventing the knock of gasoline or kerosene when used in high compression internal combustion engines. The most commonly used of these compounds is tetra ethyl lead, which, when used in quite small quantities in solution in fuels which normally knock when used under high compression, raises the critical compression to such an extent as to completely eliminate the objectionable detonation of the fuel mixture.

When the compounds heretofore known are used detonation is prevented as described above, but only when the fuel actually being exploded contains the compound in solution. I have found, however, that when amyl derivatives of lead are used, the anti-knock effect persists for a considerable time after the introduction of the derivative has been stopped and while gasoline containing no anti-knock material is being used as fuel, this result being apparently due to the deposition or retention within the cylinder of some residue of the amyl lead used or the presence therein of colloidal lead.

An investigation of this effect led to the discovery that colloidal metals alone in small quantities in fuels of low critical compressions raised the critical compressions with the elimination of knocking to a remarkable degree. Since the preparation of metallic hydrocarbon derivatives according to a method which I have discovered and describe below results in the simultaneous production of colloidal metals, which during the simple and preferred method of purification I use remain in suspension or colloidal solution in the hydrocarbon derivatives, I find it advantageous to use the derivatives containing the colloidal metals directly in the fuel with the result that the anti-knock effect of the derivatives is augmented by the anti-knock effect of the colloidal metal present originally and/or the decomposition product or products formed when the fuel is heated either by the commonly used intake manifold heater or upon compression of the mixture in the cylinders.

Various novel hydrocarbon derivatives prepared as described below decompose with separation of colloidal metals so that they serve as convenient starting points for the preparation of fuels containing colloidal metals either alone or in combination with other anti-knock substances.

The objects of the invention may, accordingly, be broadly stated to be the provision of fuels of novel compositions having high critical compressions, particularly fuels containing colloidal metals or various amyl derivatives, simple methods of preparing these fuels, and improved methods of operating internal combustion engines.

Prior to undertaking a discussion of the various fuels coming within the scope of my invention, I will describe the preparations of the various anti-knock substances which are found to be most advantageous and which result in the formation of colloidal metals as above indicated.

The preparation of tetra amyl lead will be first described. An amyl halide, or a mixture of amyl halides, is used as the source of the amyl radicals. While the various tetra amyl lead compounds differ considerably in their actions as anti-knock compounds, the tetra diethyl methyl lead, for example, being more effective than the tetra normal amyl lead, for the sake of economy mixtures of the various amyl halides obtained either from the ordinary mixture of alcohols or from the mixed pentanes may be employed. The various products are similar and may be separated together. Using commercial amyl alcohol, containing isobutyl carbinol and secondary butyl carbinol, for example, as the source of the amyl chlorides, there would be obtained a mixture of the corresponding lead derivatives.

The reaction vessel, which may be glass or metal lined with glass or enamel, is preferably provided with three spaced necks, one receiving a mechanical stirrer, another the lower end of a reflux condenser, and the third a feed funnel for the gradual addition of the reagents. It is also desirable to provide some means for heating and cooling the vessel, for example, an internal or external coil through which steam may be passed for heating or cold water, brine or liquid ammonia for cooling.

In carrying out the preparation, 24.36 parts of metallic magnesium are introduced into the vessel together with 138.91 parts of lead chloride and a few crystals of iodine which act as a catalyst in contact with the magnesium. Equivalent quantities of other reactive anhydrous lead compounds may, of course, be used.

There is theoretically required in the reaction one molecule of an ether for each atom of magnesium present. The ether used is a matter of choice, since it does not affect the character of the product, and it is found convenient to use either diethyl or diamyl ether, the proper amount of the former being 74.08 parts and of the latter 158.17 parts. Since there is necessary a solvent for the reaction products, it is advisable to use about four times the quantities of ethers mentioned. On the other hand the theoretical amount of either ether may be used and some other solvent employed. For example, if diethyl ether is used in the theoretical amount, solvents such as pentane and its isomers or amylene and its isomers may be employed either in whole or in part as solvents. If diamyl ether is used benzene, toluene or xylene may be employed, the choice of solvents being dictated by reasons of adaptability, boiling points and economy.

The ether or mixed ether and solvent are added to the materials in the reaction vessel. To the mixture the desired amyl halide is then added drop by drop or in a fine stream, 106.53 parts being added if the chloride is used, 151.04 parts if the bromide is used, or 198.05 if the iodide is used.

Usually the reaction starts spontaneously after a short time although it may be accelerated by warming. The reaction is quite vigorous and takes place with considerable evolution of heat and separation of metallic lead. It is found that the addition of amyl halide should be extended over the period of about one hour accompanied by continuous vigorous stirring in order to obtain a maximum yield. About one hour is required to complete this initial reaction.

The whole mass is then cooled by means of ice water, or, in the case of large quantities, by brine or liquid ammonia to approximately 0° C. and cold water or dilute HCl is added drop by drop or in a small stream. The reaction is very vigorous and continuous cooling is necessary. When the reaction has subsided, the tetra amyl lead is found dissolved in the ether or solvent which separates on the top of the reaction mass. Additional ether may be added to extract additional tetra amyl lead. The ethereal solution is separated, filtered, and the ether distilled, leaving impure tetra amyl lead in the receptacle. This residue is then heated to 100° C. under vacuum when a yellow solid separates. The supernatant liquid containing the tetra amyl lead is then filtered and treated with absolute ethyl alcohol. The impurities (unchanged amyl chloride, etc.) are soluble in the alcohol whereas tetra amyl lead is substantially insoluble. Accordingly, the relatively pure tetra amyl lead containing colloidal lead may be separated and dried, if desired, by treatment with anhydrous calcium chloride.

The use of dilute HCl in the reaction above is found advantageous since soluble magnesium chloride is formed rather than a cake of insoluble magnesium hydroxide which makes treatment of the mixture with solvents difficult.

As an alternative method for the recovery of the compound from the reaction mass, the ether may be distilled from the reaction vessel and the remaining material treated with low boiling gasoline (freed from sulphur compounds). The gasoline solution is then removed and the gasoline evaporated leaving impure tetra amyl lead, containing colloidal lead, which may be further purified in the manner described above.

If ether alone is used as the solvent, it is advisable to extract the residual mass in the reaction vessel with low boiling gasoline in order to recover the last traces of tetra amyl lead.

The description above refers generally to the preparation of any of the tetra amyl compounds, the only difference noticeable being in respect to the violence of the reaction, the secondary amyl halide reacting more vigorously than the normal halide and the tertiary halide reacting more vigorously than either of the preceding. The bromides are more reactive than the chlorides and the iodides more reactive than the bromides.

The reaction involved in the first step of the above process probably includes first the formation of the usual magnesium-alkyl-halide-ether compound of the familiar Grignard reactions, followed by the immediate reaction of this compound, in the nascent state, with the lead chloride present to form a complex alkyl-magnesium-lead-halide-ether compound of unknown composition with separation of metallic lead. The substance initially formed if diethyl ether and amyl chloride were employed would be $(C_5H_{11})MgCl{\cdot}O{\cdot}(C_2H_5)_2$. If amyl ether was used the compound would be $(C_5H_{11})MgCl{\cdot}O{\cdot}(C_5H_{11})_2$. In the second step of the process the alkyl-magnesium-lead-halide-ether complex referred to above is decomposed by water or dilute HCl with liberation of the tetra amyl lead $Pb(C_5H_{11})_4$.

As stated above, other than amyl derivatives may be used. For example, methyl, ethyl, propyl, butyl, phenyl or benzyl halides may be used in place of the amyl halide. Likewise other metals or elements may be used instead of lead, for example, thallium, iron or nickel. In each case the reaction takes place similarly to that described above with separation of the metal during the first step of the reaction.

If single alkyl or aryl halides are used as described above, the metal or other element will be united to a number of similar radicals only. On the other hand, mixed derivatives are obtained by using properly chosen mixtures of hydrocarbon halides. As an example of this, the preparation of dimethyl diamyl lead derivatives may be cited, the derivative in which the amyl radicals are diethyl methyl radicals, that is $(CH_3)_2((C_2H_5)_2CH)_2Pb$, being specifically chosen for illustration.

In preparing this compound the reaction is carried out in the same manner as in the preparation of the tetra amyl derivative described above except that instead of using a single alkyl derivative, a mixture of equimolecular proportions of methyl and amyl halides are used. To a mixture of 48.72 parts of metallic magnesium (preferably in the form of an alloy containing 10% copper), 277.82 parts of lead chloride, and 148.16 parts of ethyl ether (or 316.34 parts of amyl ether), together with an excess of ether or other solvent, there is added a mixture of 106.53 parts of the amyl chloride (diethyl chlor methane) and 141.97 parts of methyl idodide in the manner described above, the reaction then proceeding in the same manner as the previously described reaction, and the products being similarly separated. In these cases, also, colloidal lead is present in the products.

Instead of separation by solvents being employed, it is possible to utilize steam distillation for purification since the mixed amyl derivatives

(both methyl and ethyl) are volatile in steam. If such separation is used, the colloidal lead remains behind with the residue.

The mixed dimethyl diamyl derivative discussed is an inexpensive member of the group of metallic derivatives containing amyl radicals which have in common various desirable properties later described. The methyl halide used, which may be the chloride, bromide or iodide, and preferably the last because of its higher boiling point, is readily prepared from methyl alcohol by halogenation. In commercial production the chloride would, of course, be cheapest but requires the use of pressure apparatus. The diethyl chlor methane (or other halogen derivative) is obtained by halogenation of diethyl methane which occurs in natural gas or by the esterification by a halogen acid of diethyl carbinol.

The reaction may be varied to produce numerous other products not only by varying the alkyl or amyl derivatives used in admixture or the metal, but by varying their proportions. For example, if the product desired were monoethyl triamyl lead, one molecular proportion of ethyl bromide or other halide would be used for every three molecular proportions of amyl halide. Or, supposing dipropyl monoamyl iron to be desired, two molecular proportions of propyl halide would be used for every one of amyl halide.

The described methods differ from the well known "Grignard reaction" in that the latter is performed in two steps: first, the magnesium alkyl halide is formed and separated and secondly, this compound is treated with the material into which it is desired to introduce the alkyl radical. In the present process the magnesium alkyl halide is used in the nascent state, that is, it is formed in the presence of the substance with which it is ultimately to react. By reason of this, the time of the reaction is reduced to less than half that required by the Grignard process carried out with preformed magnesium alkyl halide and a much larger yield is obtained, due probably to the fact that the more direct reaction eliminates the formation of undesired by-products. The nascent magnesium alkyl halide is, furthermore, pure and uncontaminated by the products formed by carbon dioxide and moisture from the air, whereas the isolated halide is always rendered impure by these products prior to use.

In applying my improved reaction to the preparation of mixed derivatives, it might be suspected that the product would be a mixture of two tetra alkyl derivatives: for example, in the preparation described above, a mixture of tetra methyl lead and tetra amyl lead. As a matter of fact, however, the mixed derivative is the primary product.

While the reaction has been illustrated above in its application to lead derivatives, it will be understood that if other suitable reactive metallic salts are substituted in equivalent proportions the corresponding metallic derivatives are produced and the metal separates in the colloidal state and remains in the derivative. If this colloidal suspension is used to treat a fuel, the colloidal metal then adds its effect to that of the derivative.

The presence of colloidal metal in any one of the derivatives thus prepared is readily shown. While transparent and apparently perfectly clear after filtration, a beam of light directed through the liquid exhibits a smoky path, giving rise to the well known Tyndall effect characteristic of colloidal solutions. It appears that this colloidal metal results from the separation of the metal in the initial part of the reaction as described above, the separation possibly taking place under optimum conditions for the production of the colloidal state. A portion of the colloidal lead may also be the result of the partial decomposition of the mixed amyl lead derivatives.

The derivatives thus prepared may be added to low compression gasoline or kerosene, for example, being soluble therein, with the production of a high compression fuel. The colloidal metal remains in suspension in the mixture and adds its independent effect to the prevention of knocking.

The use of the lead amyl derivatives (either the tetra amyl derivatives or the mixed amyl derivatives) results in a peculiar phenomena. It has been mentioned above that there occurs an after effect eliminating knocking after the use of gasoline containing derivatives prepared as above. In an experiment to determine the cause for this effect, the cylinder walls and heads of an engine were cleaned and the engine operated using as fuel a gasoline which would normally produce knocking containing a small amount of tetra amyl lead prepared in accordance with the above method. Knocking was entirely eliminated. The cylinders were then opened and the walls and heads found to contain a deposit which was found under the microscope to have a metallic appearance and consist of evenly arranged particles having the appearance of small piles of microscopic shot. These deposits were removed and shaken up in highly purified gasoline which did not show the Tyndall effect. A suspension of colloidal lead which did show the Tyndall effect was thus produced. Positive tests for lead were obtained upon chemical examination of the discs. The amount of the deposit indicated that the lead deposited in the cylinder was not solely derived from that present in the colloidal state in the lead derivative but contained lead produced by the decomposition of the derivative.

Decomposition of the amyl derivatives by heat results in the formation of large amounts of colloidal lead. This is especially noticeable in the case of the dimethyl di-diethyl methyl lead described above which at 188° C. decomposes completely with separation of colloidal lead in considerable amounts. In fact, during such decomposition (produced by dropping the dimethyl diamyl lead into a tube maintained at 188° C.), the lead separating in the colloidal state exceeds the amount separating in a larger state of aggregation. Similar decompositions take place when corresponding derivatives of other metals are heated. The temperature and the time of heating markedly influence the character, the size and the activity of the resulting colloidal metal It appears that a sudden or quick decomposition yields small and very active colloidal particles which remain in suspension for a long time, whereas prolonged heating yields larger and less active colloidal particles which settle out on long standing.

In order to determine the anti-knock effect of colloidal lead, the lead produced in this manner was shaken up in purified gasoline having pronounced knocking effects and the product filtered through a fine filter. The colorless and apparently clear filtrate exhibited the Tyndall effect and when used in an engine was found

to have a high anti-knock value. Other colloidal metals, for example, thallium and nickel, exhibit similar effects.

The duration of the anti-knock effect was determined by an experiment in which 1.25 cc. of dimethyl di-diethyl methyl lead in a liter of gasoline was used in an engine. After a run, the engine was stopped and the gasoline removed. After fifteen hours the engine was operated using a fuel having knocking characteristics. Knocking was found to be entirely eliminated, due apparently, to the colloidal lead remaining in the cylinders from the previous run.

Experiments made to determine the factors limiting the ranges of usefulness of colloidal metals as detonation suppressing agents show that such usefulness depends upon the sizes of the colloidal particles. Colloidal metals may be prepared in various ways, as, for example, by subjecting the metals, such as lead, to the action of a high tension electric current while the metal is suspended in gasoline or other medium in an inert atmosphere. Varying results may be obtained by using either an ordinary induction coil or a Tesla coil (the latter providing oscillatory current at high frequency). In these cases, while colloidal suspensions have been obtained it appears that the particles in the gasoline sol are too large to exert any appreciable detonation suppressing effect.

Measurement of the sizes of the colloidal particles indicates that the particles should be of sizes (apparent diameters) between 10^{-7} cm. to 10^{-5} cm. ($1.0\mu\mu$ to 0.1μ) to exert effective action. Under the conditions of decomposition of the amyl derivatives above described, the larger portions of colloidal particles formed are within these ranges of size.

Since colloidal suspensions or sols tend to break down by the neutralization of the charges on the particles and their coalescence into larger aggregates, it may be desirable to maintain the sol in a stabilized condition by the addition of protective agents of well known type such as rubber solutions. In this fashion those sols tending to break down may be stabilized and the colloidal particles maintained in effective sizes.

The preferred fuel consists of gasoline or kerosene having low critical compression values combined with an amyl derivative of lead and containing colloidal lead. Since the amyl derivatives as a class are relatively non-poisonous, there is little danger of poisoning either of those engaged in the preparation of the fuel or of those using it. It will be clear that the amyl derivatives could be purified to eliminate the colloidal lead and could then be used alone. In this case, of course, there would be lost the additive effect of the colloid. On the other hand, colloidal lead could be used alone, being advantageously prepared by the decomposition of the lead derivatives in the manner disclosed. Or colloidal lead could be added to fuels containing, for example, tetra ethyl lead.

While more expensive, colloidal thallium, amyl derivatives of thallium, or compositions containing colloidal thallium, are similarly usable. Likewise nickel derivatives or colloidal nickel may be substituted. In all cases the colloidal metals may be advantageously prepared in effective condition by the decomposition of their amyl derivatives.

The preparation of colloidal metal by the method herein described is claimed in my Patent Number 1,805,199 patented May 12, 1931.

What I claim and desire to protect by Letters Patent is:—

1. A composition including a low compression fuel and a hydrocarbon derivative of a metal containing a diethylmethyl group.

2. A composition including a low compression fuel and a hydrocarbon derivative of lead containing a diethylmethyl group.

3. A composition including a low compression fuel and a hydrocarbon derivative of a metal containing a plurality of diethylmethyl groups.

4. A composition including a low compression fuel and a hydrocarbon derivative of lead containing a plurality of diethylmethyl groups.

5. A composition including a low compression fuel and a dialkyldidiethylmethyl lead.

6. A composition including a low compression fuel and dimethyldidiethylmethyl lead.

7. A composition including a low compression fuel, a hydrocarbon derivative of a metal containing a diethylmethyl group, and a metal in colloidal suspension.

8. A composition including a low compression fuel, a hydrocarbon derivative of lead containing a diethylmethyl group, and lead in colloidal suspension.

9. A composition including a low compression fuel and a hydrocarbon derivative of a metal containing an amyl group and a methyl group.

10. A composition including a low compression fuel and a hydrocarbon derivative of a metal containing a diethylmethyl group and a different alkyl group.

11. A composition including a low compression fuel and a hydrocarbon derivative of a metal containing a diethylmethyl group and a methyl group.

12. A composition including a low compression fuel and a dimethyldiamyl lead.

13. A composition including a low compression fuel and a compound having the formula $R_2(C_5H_{11})_2Pb$ in which the R's represent alkyl groups each of which contains less than five carbon atoms.

GELLERT ALLEMAN.