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METALLO ORGANO DERIVATIVES

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This invention relates to metallo organic compounds and to processes of making the same, and particularly to products especially adapted for internal combustion engines containing such metallo organic substances. This application is a continuation in part of application, Serial No. 111,886, filed May 26, 1926, entitled "Process of making metallo organic compounds and compositions containing the same".

Recently there has been a marked development in special fuels best known perhaps in connection with the introduction of such compounds as lead tetra ethyl into low compression fuels. Other analogous or related metallo compounds have also been suggested. However, these metallo organic compounds have usually been made by more or less classic and long known processes with but slight modification. The preparation of these compounds by such processes on commercial scale for industrial use have given rise to great difficulties in connection with the handling of the ingredients utilized and more particularly the products sought. Such compounds as lead tetra ethyl have a highly poisonous character and even in very small amounts cause untold suffering and ultimately death in the case of workers who have come into contact with it during manufacture. Such happenings have been largely responsible for the agitation recently against both the sale and manufacture of these compounds and fuels containing them.

Among the objects and advantages of the present invention is the preparation of such metallo organic compounds by processes which eliminate to a large extent many of the hazardous elements of such manufacture, and enable the materials to be handled without danger, and in fact avoid many of the steps that have heretofore been found to be necessary in their preparation.

Basically this invention involves the treatment of oils of hydrocarbon character or their derivatives so that they are converted into compounds, in part, or to a limited extent, which upon further treatment are readily converted into metallo organic derivatives. It is thus seen that the metallo organic derivatives are prepared directly in the fuel or analogous material, and preferably from constituents of the fuel or analogous material itself, without the addition of extraneous hydrocarbon sources. But this invention is not limited to such operation, since there may be added to the gasoline or other material treated, extraneous substances either for the purpose of forming the metallo organic substances within the fuel, or as a partial source for such metallo organic substances, some of the latter also being derived from the fuel or analogous material.

As the source of hydrocarbon material that may be used there may be mentioned gasolines produced by various processes and other hydrocarbon products that have fuel value. Such gasolines may be those from straight distillation processes, from cracking processes either in the presence or absence of air, from natural gas, etc. It is desirable to have present some of the lower members of the paraffin series, and consequently gasoline containing such lower paraffins such as ethane, propane, and butane are particularly desirable for treatment in this process. Further gasolines containing aromatics are also highly desirable since these are readily converted into the desired metallo organic compounds referred to in more detail below. Further, gasolines and related materials that have been produced during cracking or analogous heat and pressure treatment in the presence of air are highly advantageous, and more particularly when in such processes the gasolines produced contain even a small amount of oxygen containing substances, such as the ethers, since such oxygen containing substances often act catalytically in the processes of converting some of the described intermediate substances into metallo organic compounds.

When certain desired low members of the paraffin series are not present in the gasoline or other material to be treated, they may be added to the same; and of course similar considerations apply to any other constituents that may be desired in the final products. However, instead of converting the constituents of the gasoline or analogous material directly into the intermediate that is to be converted into the metallo compounds, there may be added to the gasoline or similar material, a substance which will be converted into the metallo compound desired, the gasoline remaining substantially as it was before the conversion and the metallo compunds being derived solely from the added substances. Any combination of these steps may be utilized depending on the products desired.

Among the metals and non-metals that may be introduced into gasoline by the processes herein set forth there may be mentioned lead, tin, silicon, antimony, arsenic, phosphorus, mercury, thallium, etc. In describing the processes illustrations will be given showing the application to the introduction of lead into the gasolines, but this is done merely as illustrative of what may be accomplished by the invention, since derivatives of the stated and other metals and non-

metals may be readily prepared by strictly analogous processes. Lead compounds are, however, those generally in use and the illustrations are accordingly drawn with this in mind. But it will be obvious that various changes may be made in this disclosure by those skilled in the art without departing from the scope and spirit of this invention.

Primarily this invention is concerned with the preparation of the desired metallo organic compound in the fuel or analogous material, so that the metallo organic compound does not have to be separately handled. The fuel may be present in a more limited quantity so that a concentrated metallo organic containing product is obtained which may be obtained by distilling off the hydrocarbon products, or which may subsequently be diluted with more fuel or gasoline or related substance to the concentration desired. Or the metallo organic substance or substances may be prepared in the gasoline or analogous material in a very dilute condition so that further dilution is unnecessary, and the special fuel is directly produced without more.

In many of the reactions of making metallo organic derivatives, the presence of catalysts have been found to be highly desirable. Such catalysts usable herein are particularly referred to as Grignard catalysts since the catalysts generally used for catalyzing the Grignard reactions may be used herein. As such catalysts there may be mentioned primary, secondary, tertiary amines and their alkyl addition products, such amines being aliphatic, aromatic or heterocyclic derivatives. Examples are aniline, dimethylaniline, carbazol, phenyl hydrazine, quinoline, etc. Other catalysts that may be used are ether, ammonia, esters, ethers in general, etc., etc. Some of these compounds may exist in the gasoline or other material undergoing treatment, so that the addition of such catalysts is not specifically necessary. On the other hand the catalysts may be added to the gasoline or analogous material, and when they are so added they may be selected from the named or other substances with regard to their value in fuel compositions. Some of the simpler ethers, and amines particularly of the aromatic series may be thus chosen.

As pointed out above, the process herein disclosed involves two essential steps, namely, first the treatment of the gasoline or analogous material to render it capable of being converted in part into metallo organic compounds, or the addition to the gasoline or analogous substance, of compounds that may be readily converted into such metallic derivatives, and second the formation of the metallo compounds therefrom. The metallic derivatives which it is desired to produce are the alkyls and aryls, such as lead tetra ethyl and antimony phenyl, and related substances. But it will be understood that when the term metallic alkyl or aryl is used, it is intended to cover the non-metallic compounds such as those of phosphorus and other non-metals, which form analogous compounds of similar properties by parallel processes.

As exemplifying one method of applying this invention, the following is given. Gasoline is given a slight treatment with halogenation agents in order to halogenate a portion thereof to introduce, say 10% of halogen. The halogens used are preferably chlorine or bromine, and the usual processes of carrying out such halogenation are used. The presence of water is desirably avoided by using dry materials. The process is preferably carried out so that mainly monohalogen derivatives are formed. It is unnecessary to halogenate but a small portion of the gasoline since the remainder will act as a solvent for the halogen derivatives formed both in this step and in subsequent operations. However, as explained above, the gasoline or analogous material may be rather completely halogenated to the mono derivatives and either then diluted, or first converted into the metallo derivatives and subsequently diluted. In the latter event a concentrate of the metallo derivatives will be obtained, or the metallo derivatives obtained without any diluting substances present.

As stated the halogenation should be carried out to give a maximum of mono halogen derivatives and a minimum of higher derivatives. Where the latter are present in undesirable amount, they may be first separated before proceeding to the formation of the metallo derivatives, as by distillation. Among the halogenation processes available and well known in the art for producing the halogenation of the gasoline or related material in accordance with the present disclosure, reference may be made to the U. S. patents to Brooks, 1,191,916; Blanc, 1,248,065; and Sparre, 1,379,367, which patents disclose methods that may be employed for halogenating gasoline. The procedures of these patents or other patents well known in the art, and well known methods of the art for producing halogenated products and particularly from gasoline and related material may be employed.

Instead of proceeding in this way, the desired amount of a halogen derivative may be introduced into the gasoline. For example, ethyl chloride, methyl chloride, propyl bromide, etc. may be added to the gasoline or analogous material in the desired proportion to yield the requisite amount of metallo derivatives in subsequent operations.

It should be noted that in the final fuels containing such metallo derivatives, they need be present in but small amount only, for example less than one percent, and even less than one-quarter of one percent. Consequently whether the halogen derivatives are formed in the gasoline or analogous material directly by halogenation processes, or whether desired halogen compounds are added thereto, they need be present in but small quantities if desired, for example in such quantities as will yield the requisite proportions of metallo compounds by further reaction desired in the final fuel. But it is found to be preferable to produce the halogen content above that finally desired, convert such halogen content into the metallo derivatives, either partially or completely, and having thus produced a concentrated metallo content in the fuel composition, dilute this when desired to the final composition sought.

Further, as indicated above, it is well to choose gasolines or analogous material that contain a substantial proportion of the lower paraffins, or to enrich the gasolines with such lower paraffins or their derivatives, in order to form a preponderant amount of the lower metallo alkyls. This is well taken care of in view of the fact that in most of the reactions used for forming the metallo derivatives, the lower paraffins react much more readily than do the higher ones, so that it is possible to control the reaction and produce more of the lower metal alkyls, than of the higher ones. Instead of enriching a gasoline with lower paraffins, it may be enriched with aromatics such as benzene, toluene, xylene, etc. when these are not

present, and if they are desired, in order to form the metal aryls in the fuel.

Having thus produced a halogen derivative content in the gasoline or analogous material of desired amount, the solution preferably without water present, is subjected to any well known process for converting the halogen derivatives into metal compounds, such conversion taking place directly in the fuel itself, any excess of the latter not halogenated forming a solvent. When desired, some additional fuel may be added as solvent, or extraneous solvents may be added both for their solvent purposes and also for action as catalysts.

Two methods particularly may be used at this point for a conversion of the halogen derivatives into metal compounds. The halogen compounds may be converted into their corresponding magnesium compounds (Grignard reagents) and then reacted with heavy metals, their alloys, or compounds such as salts, in order to form the metal derivatives; or the halogen derivatives may be treated with metallic substances, their alloys, or compounds to form the desired metal derivatives in the fuel. These reactions are preferably carried out in the presence of catalysts and sometimes in the presence of reducing agents in order to eliminate certain side reactions or by-products, and desirably the presence of water in substantial amount is avoided. Several examples will be given, it being understood that these are merely for purposes of illustration, and are not limiting in any way, since the invention is capable of application in a wide variety of ways.

The halogen derivatives contained in the fuel substance is subjected to the action of magnesium desirably in the form of wire or band. Such magnesium may be either immersed in the fuel mixture, or the latter may be circulated through a bed of magnesium until the halogen content of the fuel substance has been converted into the magnesium compound in accordance with the following equation:

$$RCl+Mg=RMgCl$$
$$RBr+Mg=RMgBr$$

where R stands for either an alkyl or an aryl radicle. In carrying out the conversion of the halogenated material into the metal Grignard reagent, it is not necessary to convert all of the halogen compounds into magnesium compounds, but any desired proportion of the halogen derivatives may be allowed to remain therein within the limits sought, since in the special fuels containing such compounds as lead tetraethyl it is desirable to have present halides, such as the chlorides and bromides, in the final fuel as it is consumed in the internal combustion engine for example in order to prevent the deposition of lead in the engine. Consequently the process can be so carried out that considerable quantities as desired of the halides remain in the fuel. Or when making metallo organic concentrates as described above, a considerable portion or all of the fuel remaining unconverted into the metal derivatives, may be in the form of halides which can then be diluted with more fuel to obtain the final product ready for use.

Among the methods which may be employed for producing the desired metallo organic derivatives, specific reference may be made to the process abstracted and referred to in Chemical Abstract, vol. V, at page 2639, and particularly the method therein disclosed for producing these metallo organic combinations in the presence of such organic material as ligroin, benzene, etc.

The Grignard type of reagents having been prepared as set forth above, it is then treated to form the desired metallo compound by reaction with desired heavy metal or non-metal compounds. For example, in the preparation of lead tetraethyl the alkyl or aryl magnesium halides contained in the fuel mixture, may be reacted with a lead salt such as the chloride to form the corresponding lead compounds. One equation illustrating the reactions that take place in such processes is the following:

$$PbCl_2+4C_2H_5MgBr=Pb(C_2H_5)_4+MgBr_2+2MgBrCl+Mg$$

Or again the following will illustrate the reaction:

$$2PbCl_2+4C_2H_5MgBr=Pb+Pb(C_2H_5)_4+2MgCl_2+2MgBr_2$$

These equations are merely given to illustrate several reactions that may take place and being theoretical only are not intended to be limiting. Other metals yield corresponding compounds as well of the alkyls as of the aryls.

In view of the fact that the lower paraffins more readily form the metal alkyls, the reaction can be controlled so that more of the lower metal alkyls are present than are the higher alkyls; and a similar control can be exercised in the halogenation reactions to limit the halogen derivatives formed largely if not entirely to the lower paraffins; or similarly this result may be reached by the addition of halides to the desired gasoline or fuel, using the lower alkyl halides only.

Other metal salts or compounds may be used to obtain similar reactions and the production of corresponding metal organic derivatives in the fuels. And analogous reactions may be produced with non-metal compounds. As pointed out above, catalysts are desirably used in most of these reactions, and as such the catalysts may be added compounds, particularly those that have a value in the final fuel composition, or merely solvents such as ether which also exert a catalytic influence. When as frequently happens, some of the byproducts are insoluble in the fuel, they may merely be filtered out. But if desired, they may be washed out with water or other washing solutions.

Instead of making the magnesium derivatives from the halides, the later may be used directly without forming the magnesium derivatives in the presence of magnesium, ether or other appropriate solvents and catalysts. The intermediate step of forming the magnesium is thus eliminated. Further in place of using magnesium, zinc may be used to form intermediate compounds which may be used in an analogous manner.

And still further, the methods of reacting the halides with lead, lead alloys, or lead compounds may also be used without forming magnesium or corresponding derivatives at all. For example, the fuels containing the halides may be treated with lead or lead alloy (sodium alloy containing from about 6 to 20 percent of sodium) in the presence of reducing agents and catalysts. In these reactions the temperatures are generally maintained between 20 and 36° C. unless pressure is employed in which case the higher temperatures may be used. When not using pressure, the upper limit of temperature is largely controlled by the boiling points of the fuel ingredients. And the reaction products are often

washed with strong alkali to improve the yields of the desired metal alkyls. When lead or other metals, or their alloys are used, these are preferably used in a more or less finely divided condition to increase the surface contact. The reduction reaction may be effected due to the reaction of the sodium in the alloy for example, with a small amount of water added to the materials undergoing treatment. But reduction may be carried out in any other desirable way.

Depending to a large extent on the amount of halides present undergoing reaction in such compositions, the temperature control will vary. If large quantities of the halides are present, the temperature may rise so that cooling is necessary to keep it within the prescribed limits. But where the amount of halides is small in comparison with the solvent or fuel elements present, heating may be required to a limited extent to raise the temperature.

In any reactions where the halides or the magnesium or similar Grignard reagents are used, and contacted with metals, their alloys or salts or other compounds, instead of adding the metals etc. to the fuel containing the halides, the fuel, etc. may be circulated through a chamber containing the metals, alloys or etc. until the desired degree of reaction has been obtained.

While a number of metal derivatives may thus be introduced into the fuel by being made directly therein, if desired after the production of one metallo organic compound, it may be converted either partially or wholly into other metallo compounds. And furthermore, if desired, instead of converting the Grignard intermediates produced as set forth above, or added to the fuel—for example, the Grignard reagents might be prepared in the usual manner and then added to the gasoline or other fuel—the latter may be converted into other derivatives than the metallo derivatives. The Grignards are well known as excellent intermediates for the synthesis of a number of organic compounds. So that they may be used as set forth herein to form a large number of organic compounds that have value in fuels. For example, by appropriate treatments they may be converted into alcohols, phenols, aldehydes, ketones, etc., and these reactions may be utilized so that a portion of the Grignard reagents are converted into the metallo derivatives and a portion into other organic compounds.

And further, many of the products may be made in the fuel from the halides by taking crude hydrocarbon materials that must be subjected to distillation or other treatment, or treatments, in order to obtain motor fuels from them, by adding the requisite materials to them to form the metallo compounds, or converting a portion of such crude materials into compounds that will form metallo derivatives, and then carrying out the distillation or other treatment, so that a gasoline or analogous material or fuel is obtained containing the metallo organic compounds that have been formed during the distillation or other treatment, which may or may not have been carried out under pressure.

Whenever desired, any material to be treated in accordance with the hereinabove set forth disclosure, may be dried if desired or necessary in order to remove any excess moisture that might be present and might interfere with the progress of the particular reactions sought in the production of specific compounds.

In carrying out the processes set forth herein, the reacting ingredients may be used in their theoretical molecularly equivalent proportions in accordance with the equations for the reactions as illustrated hereinabove, or an excess of any of the stated ingredients as compared with the material with which it reacts may be employed. Thus when the halogenated gasoline is reacted with the magnesium, the materials may be present in equivalent molecular amounts, but preferably the halogen derivative is used in excess. So too, when the Grignard reagent is formed, the material with which it is reacted is desirably used in slight excess.

Ordinarily as a result of this process, a complex mixture of organic derivatives of a stated metal, or metalloid is obtained, the derivatives, however, usually containing a number of closely related derivatives. Thus in a given instance, in making lead tetraethyl, there will also be present lead derivatives of other alkyls. And usually there is no necessity for isolating individual compounds, since these complex mixtures of such derivatives are desirably present in motor fuels for example, since they modify the action of each other having solvent action on each other, and hydrocarbons and their derivatives to yield homogeneity, smoother explosion curves, etc.

The metallo derivatives may be recovered as such by evaporation of hydrocarbons etc. from the reaction mixtures, or in any other desired way; or they may be diluted as with fuel ingredients for direct use.

While lead tetraethyl has been specifically referred to, antiknock metallo organo derivatives other than (and when desired to the exclusion of) lead tetraethyl, may be produced.

Having thus set forth my invention, I claim:

1. The method of making metallo organo derivatives which comprises treating gasoline to produce halogenated aliphatics therein convertible into metallo organo derivatives, and reacting such halogenated aliphatics under conditions to produce metallo organo derivatives with a metallic component to produce metallo organo derivatives the metallic component containing a metal of the anti-knock type, whereby the metallo organo derivatives possess anti-knock properties.

2. The method of making metallo organo derivatives which comprises treating a hydrocarbon oil with chlorine to form chlorides dissolved in the hydrocarbon oil, reacting such chlorides with magnesium to form Grignard bodies within the hydrocarbon oil, and then treating said Grignard bodies with a lead salt to form lead derivatives of the hydrocarbons.

3. A product containing a complex mixture of metallo organo derivatives the organic radicals of which correspond with the organic radicals of a group of hydrocarbons of a hydrocarbon oil.

4. A product containing a complex mixture of organic lead derivatives the organic radicals of which correspond with the organic radicals of a group of hydrocarbons of a gasoline.

5. A process of making anti-knock compounds which comprises halogenating petroleum hydrocarbons, and reacting such halogenated petroleum hydrocarbons with metallic reactants under conditions to form a mixture of anti-knock compounds of the metallo organic type, the metallic reactants containing a metal of the anti-knock type, whereby the metallo organo derivatives possess anti-knock properties.

6. A process of making anti-knock compounds which comprises metallizing a complex mixture of petroleum hydrocarbons containing halogen derivatives by reacting said mixture with metallic

components to form metal containing anti-knock compounds from constituents of said mixture.

7. The method of making metallo organo derivatives which comprises treating a hydrocarbon oil with a halogen to form halides dissolved in the hydrocarbon oil, reacting such halides with magnesium to form Grignard bodies within the hydrocarbon oil, and then treating said Grignard bodies with a heavy metal compound to form heavy metal derivatives of the hydrocarbon the heavy metal compound containing a metal of the anti-knock type whereby the heavy metal derivatives of the hydrocarbon yield anti-knock properties.

8. The method of making metallo organo derivatives which comprises treating a hydrocarbon oil with chlorine to form chlorides dissolved in the hydrocarbon oil, and reacting such chlorides with lead alkali metal alloy to form lead derivatives of the hydrocarbons.

9. The process of preparing gasoline containing lead compounds which comprises reacting chlorine with gasoline to form chlorinated hydrocarbons therein, and treating the gasoline containing the chlorinated hydrocarbons with lead sodium alloy to convert the chlorinated hydrocarbons to hydrocarbon compounds of lead.

10. The process of preparing gasoline containing lead compounds which comprises reacting chlorine with gasoline containing dissolved, normally gaseous, hydrocarbons to form chlorinated hydrocarbons therein, and treating the gasoline containing the chlorinated hydrocarbons with lead sodium alloy to convert the chlorinated hydrocarbons to hydrocarbon compounds of lead.

11. The process of preparing cracked gasoline containing lead compounds which comprises chlorinating the gasoline with chlorine, to form chlorinated hydrocarbons, and treating the chlorinated hydrocarbons with lead sodium alloy to form hydrocarbon compounds of lead.

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