

UNITED STATES PATENT OFFICE

2,272,134

MODIFIED MOTOR FUEL AND PROCESS OF
MAKING SAME

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8 Claims. (Cl. 44—9)

This invention relates to motor fuels and to methods of producing the same, and particularly to such motor fuels containing anti-oxidants, anti-knock ingredients, anti-gumming agents, dyes, etc., as well as processes of making the same, and particularly where such modified motor fuels are produced from the motor fuel itself by appropriate chemical or other treatments, whereby anti-oxidants, anti-knock ingredients, anti-gumming agents, dyes, etc. are produced in situ in the motor fuel from ingredients in part, at least, present therein.

In the prior art there have been various suggestions for modifying motor fuels, particularly of the hydrocarbon type by the addition of agents usually produced from extraneous sources for the particular purposes in hand, such as anti-knock derivatives or either the metallo or non-metallo type, or anti-gum ingredients of various types, or dyes have been incorporated into such motor fuels for the purpose of characteristically coloring them, such dyes having been produced extraneous of the motor fuel and added thereto. The separate production of such added materials is both burdensome, undesirable and expensive. Thus, in the production of the metallo anti-knock compounds, of which tetra ethyl lead is probably the best known and most widely used, the production of tetra ethyl lead outside of the motor fuel and its subsequent incorporation therein, requires the manufacture and handling of the very poisonous metallo organo derivative. Furthermore, one is thus limited to the use of individual, or at best a mixture of closely related derivatives of one or two such compounds only, which are not always found compatible with the ingredients of the motor fuel. Again, in connection with the addition of dyes to motor fuels in order to color the same, the dyes are the usual types of dyes produced outside of the motor fuel and incorporated therein. Difficulties have been encountered in obtaining dyes that are compatible with the motor fuels, or preferably soluble therein. And the dyes available have been very limited in character for this reason.

Among the objects of the present invention, therefore, is the production of motor fuels or hydrocarbon derivatives utilizable for motor fuel purposes, or for the production of motor fuels therefrom, in which anti-oxidants, anti-knocking ingredients, anti-gumming agents, dyes, etc. are produced in the motor fuel or hydrocarbons, preferably from ingredients already present therein by appropriate chemical reactions.

Other objects include the production of such

motor fuels or hydrocarbon materials containing novel components for anti-knock or anti-gum or dye purposes, without necessarily being produced from the motor fuels themselves.

Other objects and advantages will appear from the more particular description given below, it being understood, however, that this more particular description is given by way of illustration and explanation only, and not by way of limitation, since modifications thereof may be made by those skilled in the art without departing from the scope and spirit of the present invention.

The present application is concerned with the preparation of metallo organic and other derivatives 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 is particularly emphasized, the oils of hydrocarbon character or their derivatives or fractions or distillates being converted into compounds in part, or to a limited extent, which upon further treatment are readily converted into the metallo organo and other derivatives. In addition, extraneous substances, either for the purpose of forming the metallo organic substances within the fuel, or as a partial source for such metallo organic and other substances, some of the latter also being derived from the fuel or analogous material, may also be added to the gasoline or other material treated.

The hydrocarbon materials treated may be the hydrocarbon oils, their fractions and distillates including the gasolines, produced by various processes and other hydrocarbon products that have fuel value. Such gasolines, for example, may be those from straight distillation processes, from cracking processes either in the presence or absence of air, from natural gas, etc. As pointed out, where the metallo organo derivatives are to be produced of the alkyl type, it is desirable to have present in the gasolines or other hydrocarbon product, lower members of the paraffin series, and consequently gasolines containing such lower paraffins, such as ethane, propane and butane are particularly desirable, but the gasolines containing aromatics also are readily converted into the desired metallo organic compounds. Gasolines and related materials 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. The presence of such oxygen-containing compounds as the aldehydes, ketones, etc. are desirable for other purposes set forth below.

If certain desired lower members of the paraffin series are not already present in the gasoline or other material to be treated, they may be added to the same; and of course the same applies to other constituents that may be desired in the final products. 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 compounds being derived solely from the added substances, or any combination of these steps may be utilized.

Among the metals and non-metals that may be introduced into gasoline by the processes there set forth, there may be mentioned lead, tin, silicon, antimony, arsenic, phosphorus, mercury, thallium, etc. Lead compounds are particularly used for illustrative purposes therein in view of the wide use of lead compounds.

In the preparation of the metallo organic compounds in the fuel or analogous material, the metallo organic compounds do not have to be separately handled. The production of such metallo organic compounds in the fuel and from fuel constituents may be carried out so that the fuel is present in a more limited quantity whereby a concentrated metallo organic containing product is obtained which may be secured by distilling off the hydrocarbon products present, 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. The preparation of the desired ingredients in very dilute condition is particularly desirable where some of the constituents thus produced are not very soluble in the motor fuels, although the very small quantities of such materials present needed for anti-knock, anti-oxidant, anti-gum, or dye purposes, etc. do not require absolute solution, although in such dilutions in which they are used, they are readily obtainable in solution form, or if necessary blending agents may be utilized to produce the requisite solubility.

In many of the reactions of making metallo organic derivatives, the presence of catalysts have been found to be highly desirable, such catalysts particularly referred to as Grignard catalysts are particularly referred to, including for example, 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 desirable catalysts or agents that may be present include ether, ethers in general, ammonia and its derivatives, esters. These compounds may exist in the gasoline or other material undergoing treatment, so the addition of such catalysts is not specifically necessary. And this is particularly true in connection with the gasolines produced by oxidation processes, including both those of the vapor and liquid phase oxidation reactions.

Other compounds, like the amines, etc. referred to above may be present in the gasoline by various methods, as indicated below, wherein they may be produced from constituents of the gasolines themselves, or may be introduced from external sources. The catalyst added may be selected from the named substances or other derivatives, particularly with regard to their value in fuel compositions, for example, the simpler ethers, and the amines, particularly the aromatic series thus being indicated.

Metallo organo derivatives as utilized herein may be produced in a variety of ways, as for example, by the methods disclosed in Patent No. 2,012,356, granted August 27, 1935, entitled Metallo organo derivatives.

While in the production of Grignard reagents monohalogen derivatives are particularly emphasized, where the halogen derivatives are converted into amines or other derivatives, higher halogen derivatives are desirable leading to the production of diamines, etc., which diamines, particularly the aromatic diamines, like paraphenylenediamine, are particularly valuable as in the production of dyes, etc.

The Grignard catalysts referred to above, such as the aromatic amines, like aniline and dimethylene, carbazol, etc., the aliphatic amines, like phenyl hydrazine, and the heterocyclic derivatives, like quinoline, will also be present in the motor fuels, except as they may in part be altered by the reactions to which the fuel fractions are subjected, and to the extent that they are present are desirable ingredients as anti-gum agents, etc.

It will be seen that in these reactions, metal is precipitated, which may be either magnesium or lead as illustrated above. Such precipitated metal formed by these chemical reactions is obviously in finely divided condition, and since they need not be removed from the fuel will lend their own anti-knock qualities to the motor fuel, particularly when used in combination with the alkyl and aryl metallo derivatives.

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 partially or wholly into other metallo compounds. And furthermore, if desired, instead of 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 in the prior description 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.

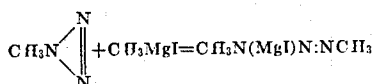
And further, many of the products may be made in the fuel from the halides by taking crude hydrocarbon materials that must be subjected to distillation or other treatment, or treatments, in order to obtain motor fuels from them, by adding the requisite materials to them to form the metallo compounds, or converting a portion

of such crude materials into compounds that will form metallo derivatives, and then carrying out the distillation or other treatments, 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.

Thus the introduction of the halogen to the material undergoing distillation will yield halogenated fractions as, for example, halogenated motor fuel fractions which may accordingly be treated as set forth above. Or the introduction of halogen followed by contact of the halogenated product with the sodium lead alloy, for example, before distillation, or at various stages thereof, will result in fractions such as motor fuels produced with the metallo derivatives in the fuel during the distillation.

The Grignard reagents, as indicated above, are utilizable however in many other directions for the production of both metallo derivatives other than those of the alkyl and aryl types strictly, and also for the production of many valuable ingredients in motor fuels which do not necessarily contain any metallo component.

Thus, they may be utilized for the production of diazo compounds, both of the aliphatic and aromatic series, and such diazo derivatives are important components in the motor fuels, whether or not they contain metallic derivatives, both varieties of which will be illustrated below, namely those containing metallo components, and those free from them. Diazo components are valuable in the motor fuels from two standpoints. Both because they have properties as anti-gum derivatives, and also because they increase the power obtained from motor fuels. The contents of such diazo compounds in motor fuel may be very low, not running more than 1% in any event, and substantially smaller proportions, as low as .1% in the motor fuels giving markedly increased and valuable properties thereto. For example, derivatives of the diazo amino paraffins are readily prepared, for which purpose the alkyl Grignard reagents may be reacted with the alkyl azides, of which the following reaction is exemplary:



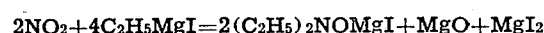
And as a result of which reaction there is produced compounds corresponding with the magnesium salt of diazo amino methane. In the application of such reactions herein, there will usually be produced complex derivatives of such components. The magnesium derivative produced in accordance with the preceding method, may be permitted to remain in the motor fuel itself, or may be treated as a Grignard for other reactions, such as those to which the Grignards are capable, particularly as emphasized above. Thus various metallo derivatives may be produced, such as the copper compound:



or other metallic derivatives, such as those of lead, etc. may similarly be produced and utilized in the motor fuel, both because of the lead component, and also because of the diazo grouping present. While the alkyl derivatives have been particularly referred to, diazo aryl derivatives may be produced in an analogous way, and particularly diazo amino paraffins, and diazo amino

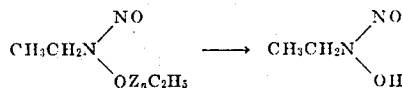
aryls. And while such reactions and the production of such derivatives may be carried on outside of the motor fuel, and the diazo compounds or derivatives added to the motor fuel, desirably the compounds are produced within the motor fuel from components thereof, such as by halogenation, conversion into Grignard reagents, as set forth above, and then treatment with azides in accordance with the preceding methods, and produced from the components of the motor fuels themselves result in complex derivatives that desirably flux each other, and remain in homogeneous combination with the motor fuel constituents themselves. Further, as noted above in connection with metallo derivatives generally, the reactions may be carried out utilizing the motor fuel as a diluting agent, so that the compounds are produced in only smaller quantities, namely in the amounts in which they must be present in the final motor fuel, or the materials may be produced in the form of concentrates, and subsequently diluted with additions of motor fuel constituents to produce compositions containing the final minor quantities of such ingredients.

Similarly, the Grignard reagents may desirably be employed for the production of both metallo and non-metallo derivatives of the hydroxyl amines. The hydroxyl amines, including hydroxylamine itself ($\text{OH}.\text{NH}_2$) are desirable ingredients in motor fuel compositions as anti-gumming agents. And these derivatives may accordingly be prepared from the motor fuel components themselves, or if desired may be added to the motor fuel from extraneous sources. Utilizing the Grignards for the production of the hydroxyl amine derivatives, the following is illustrative. The Grignards produced in the motor fuel in accordance with reactions set forth above are caused to react with nitrogen oxides. Thus ethyl magnesium iodide by the action of nitric oxide is converted into derivatives of the beta-dialkyl hydroxylamine type in accordance with the following illustrative equation:



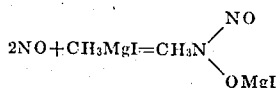
and such derivatives may be treated in various ways. They may be permitted to remain in the motor fuel in that form without further treatment, or they may be converted into lead or other metallic derivatives as by reaction with the lead compounds, as set forth above, for the other Grignards, producing for example the lead compound: $[(\text{C}_2\text{H}_5)_2\text{NO}]_2\text{Pb}$. Or they may be decomposed with water to give the beta-dialkyl hydroxylamine derivative. It will be noted that nitroso derivatives are produced, as set forth above, and such nitroso derivatives are also important components of the motor fuel, in view of their anti-gum properties.

Nitroso beta-alkyl hydroxylamine derivatives may similarly be prepared by the action of nitric oxide on zinc ethyl and subsequent decomposition by water in accordance with the following equation:



As illustrative of the production of metallic derivatives of such nitroso hydroxylamine derivatives, the following will also serve in addition to that set forth above, wherein the alkyl Grignard is reacted with nitric oxide, and the resulting

compound converted into metallic salts, such as those of copper, lead, etc.:

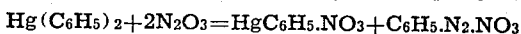


the copper salt having the formula $(\text{CH}_3\text{N}_2\text{O}_2)_2\text{Cu}$ and the lead salt the following formula



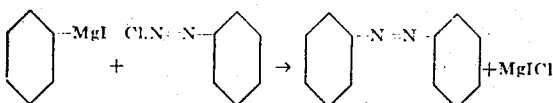
Furthermore, since these alkyl hydroxylamines are readily reduced, they may by such reduction reactions be converted into the corresponding amines, the beta-hydroxylamines thus yielding dialkyl amines. Such amine derivatives are very desirable components in the motor fuels, because of their anti-gumming characteristics. And by these means the production of amino derivatives of the paraffin character may desirably be produced in the motor fuels. Of course, the reactions when produced in the motor fuels themselves result in complex mixtures of such derivatives, and both alkyl and aryl derivatives may thus be obtained.

The production of diazo paraffin derivatives has been illustrated above, and reference may also be given to the production of diazo aryl salts by analogous methods. For example, by the action of nitrous fumes on the metallo diaryl derivatives of which the following is exemplary:



And both of the produced components, and particularly the diazo salt, are valuable constituents of the motor fuel. The production of the diazo salt of the aryl type, for example, of course, have merely been exemplified in the benzene diazo nitrate referred to above, and other types of derivatives, such as para-diazo-toluene nitrate may be similarly produced, for example, from mercury para-ditolyl, while other aryl derivatives of similar type may be produced, as well from the mercury derivatives as the other metallo aryl derivatives.

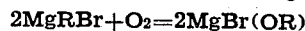
The metallo aryl Grignard reagents may also be desirably employed in the production of azo compounds, for example, benzene magnesium iodide yielding with benzene diazonium chloride, azo benzene in accordance with the following reaction.



Such azo compounds are desirable components in motor fuels, and these types of reactions of which that illustrated is merely exemplary may be utilized in the production of azo dyes in the motor fuels from constituents thereof, as more fully explained below. In this connection it may be pointed out that the Grignard reagents are easily produced in the motor fuel from constituents thereof as set forth above, and the diazo compounds may also be produced herein both by methods explained above and by subsequent methods, and such constituents produced in the motor fuel then permitted to react to produce the azo compounds. Substituted azo compounds of the true dye type may thus be produced in the motor fuel, and in view of their production in complex mixtures in such motor fuel from derivatives thereof, dyes can be produced in the motor fuel that remain in solution therein, which is difficult in the production of many types of

dyes by extraneous reactions, followed by their incorporation into motor fuels. Entirely new varieties of dyes in complex mixtures are thus producible in the motor fuel from constituents in this way. The Grignard reagents may be produced from the motor fuels themselves, and reacted with diazo salts produced outside of the motor fuels, or as noted above, the diazo salts may also be produced in the motor fuels, or a portion thereof for reaction with the Grignard reagents. Or, as explained below, the diazo compounds may be produced from the motor fuel constituents themselves and reacted with Grignard reagents from external sources.

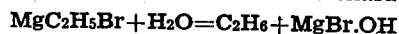
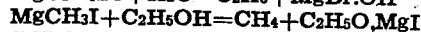
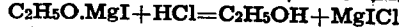
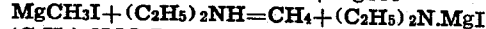
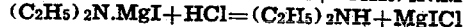
Other reactivities of the Grignard reagents may, of course, be utilized to produce various types of organic derivatives, and are particularly valuable where complex mixtures are thus obtained because of the production of the Grignard reagents in situ in the motor fuels from constituents thereof. Thus the Grignard reagents absorb dry oxygen to give intermediate derivatives, which upon treatment with mineral acids result in alcohols or phenols, and when such reactions are employed in accordance with the present invention complex mixtures of such derivatives are produced in the motor fuels. The treatment with mineral acid may be carried out by agitating the hydrocarbon phase containing the desired Grignard derivative with an aqueous mixture of mineral acid, such as hydrochloric acid, for example, until the desired reaction between the water and hydrocarbon phases is produced, or the hydrogen chloride may be dissolved or absorbed in alcohol, and the latter utilized in the reaction. The processes may be formulated in accordance with the following equations:



in which reactions R represents either alkyl or aryl, depending on whether alcohols or phenols are produced.

Or the Grignards may be permitted to absorb carbon dioxide, and subsequently treated with mineral acid in the manner set forth immediately above to produce carboxylic acids, or their derivatives. If the halogenation treatment prior to the production of the Grignard reagent is carried out on a gasoline which has first been aminized so that amino aryls are present, these reactions may be utilized to produce amino benzoic acid and related compounds, particularly in complex mixture in the motor fuels produced in situ from constituents of the motor fuels themselves, and these derivatives are also desirable as anti-gum materials.

The Grignard reagents may further be reacted respectively with water, alcohols and primary and secondary amines to produce hydrocarbons and other derivatives, and the Grignard reagents produced as a result of such reactions when treated with mineral acids by methods explained above may be converted into corresponding alcohol and secondary amine derivatives, which are thus producible in the motor fuel itself from constituents thereof. The following equations will illustrate reactions of this character:



In carrying out such reactions as those referred to above, and as noted above in connection

with other reactions where aqueous mixtures are utilized, such as the mineral acids, such water phase containing the acid may be agitated with the hydrocarbon material, or the acids may be dissolved in alcohol or other organic solvents, and the latter utilized to produce the desired conversion.

The production of various amines and their derivatives, such as the hydroxyl amines have been given above derivable from the Grignard types of reagents. Various other methods for producing the amines and their derivatives in the motor fuels from constituents thereof may be utilized.

Thus the chlorhydrocarbons produced by the halogenation of the gasoline fraction, for example, may be treated in situ with ammonia, preferably under pressure, or sodamide may be utilized to react with the chlorhydrocarbons to produce the amines. Other methods involve the nitration by nitric acid or mixtures of nitric and sulphuric acids applied to the gasoline fraction to produce nitro derivatives in the motor fuel itself, followed by reduction as by means of the usual reducing agent, such as powdered zinc and acids to produce amino derivatives directly in the product.

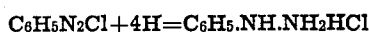
The nitroparaffins instead of being directly reduced to the amines in the manner set forth above, may be converted into the beta-alkyl or aryl-hydroxyl amines by reduction with stannous chloride, or with zinc dust and water, or by electrolytic reduction, yielding various varieties of the beta alkyl or aryl hydroxyl amines in the motor fuels themselves.

Reduction of the nitroso compounds derived through the Grignard and similar reactions as set forth above also yield amines. The presence of amines in the motor fuel may be utilized very desirably for conversion into other derivatives of great import in the motor fuel. This has been in part indicated above by the production of various compounds including the diazo or diazonium salts. But once the motor fuel has been aminized by any of the methods set forth above, or by other methods, as for example, where phenols have been produced in the motor fuel by reactions set forth above, such motor fuel containing phenols may be heated under pressure with ammonia, or preferably with the ammonium compound of zinc chloride or of calcium chloride, naphthol, for example, in this way yielding naphthylamines.

Other means of producing the amines particularly in cyclic and aromatic compounds include the treatment of the halogenated gasoline fractions with aluminum chloride by the Friedel and Crafts reaction to produce cyclic and aromatic compounds. And these may then be heated with sodamide above 200°, hydrogen being evolved, and the amines being produced. For example, heating naphthalene with sodamide above 200° C. yields alpha-naphthylamine.

The diazo salts or diazonium salts may be reduced to produce phenylhydrazine derivatives and related compounds, and since this may be readily carried out in the motor fuel itself from diazo compounds produced as noted above, these hydrazine derivatives are readily produced from components of the motor fuel in situ. Thus, for example, phenyl diazonium chloride reduced in this manner yields phenylhydrazine hydrochloride from which the base may be separated by

washing with dilute alkalies. The process may be formulated in the following reaction:



Once the amines have been produced in the motor fuel, or are present therein, and they may, of course, be added from extraneous sources for this purpose, but desirably they are produced in complex mixture in the motor fuels themselves by any of the methods set forth above, they lend themselves to a wide variety of treatments for the production of various types of derivatives of great importance in the motor fuels, since they may be readily converted into anti-gum components, dyes, etc.

One of the most important methods for deriving desirable components therefrom is by treatment with nitrous acid or its salts and esters. Under such treatments the aliphatic amines in the fuel are converted into alcohols, which are, of themselves, important components of the motor fuel mixtures for various purposes, while the aromatic and cyclic amines are converted into diazo derivatives, which lend themselves to various treatments, such as reduction, coupling, etc.

Various methods for producing such diazonium derivatives and alcohols by the utilization of nitrous acid, its salts and esters are, of course, available. While diazotization is usually carried out at low temperatures in aqueous solution, it is not necessary that aqueous solutions be employed, although they can be applied in manners analogous to that set forth above for other reactions involving the use of aqueous solutions. For example, the motor fuel containing the aminized derivatives may be agitated with the nitrous acid solution, whether produced from the salts or from the esters, so that the aqueous phase is in continuous contact with the hydrocarbon phase. And conversion of the amino derivatives is accordingly accomplished. In order to avoid loss of desirable products into the water phase, however, the reactions are desirably carried out in non-aqueous media. The presence of the alcohols formed by the action of the nitrous acid on the aliphatic amines is important in such reactions, since such alcohols act as a satisfactory medium in which the diazotization may be carried out.

Thus absolute alcohol may be saturated with nitrous fumes, and the saturated alcohol then added to the aminized motor fuel with the resulting production of diazo compounds. Other methods include the addition of absolute alcohol or ether, if desired, but they are not essential to the aminized motor fuel, and then passing dry hydrogen chloride into such solution, heating to 40 or 50° until the last traces of acid are removed. The theoretical quantity of amyl nitrite is then added, and this can even be done at ordinary temperatures, although lower temperatures are usually preferable in the production of diazo compounds, particularly where wide varieties of such diazo compounds are formed as is true in the treatment of aminized motor fuels, some of the diazo compounds only being stable at lower temperatures, as around 0°. The diazo compounds are thus formed in the motor fuel fraction from components thereof.

It should be kept in mind, as pointed out above in connection with other types of compounds and methods, that it is not necessary to treat the entire fraction of gasoline in this manner, but only a portion thereof may be subjected to such reactions, and after the production of the diazo

compounds, such fractions added to the remaining portion of the motor fuel. Or the diazo compounds may be produced in concentrated condition, and then diluted with the motor fuel constituents to produce the final fuel. The diazo compounds, while sometimes insoluble, will usually be found to be present in solution because of the complex derivatives obtained from the treatment of the motor fuels themselves, in which the various ingredients flux each other, and produce a homogeneous composition. But where minor quantities of the diazo compounds in high dilution are utilized, the suspension of such diazo compounds in the motor fuel components also produce compositions that may be utilized directly.

Nitrosyl bromide and nitrosyl chloride, as well as nitro sulphonic acid may also be employed for the production of the diazo compounds. Thus the aminized motor fuel, either with or without alcohols present, or introduced for that purpose, has added thereto an alcoholic solution of hydrogen chloride containing 2.5-3.0 mols of acid as compared with the amines present. The composition is cooled in ice, and a solution of nitroso chloride, for example, in toluene added. The diazo salt is thus produced.

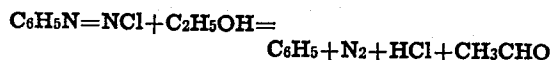
The diazo salts may also be produced from the nitroso aryl hydrazine referred to above by passing nitrous fumes into the solution of the nitroso aryl hydrazine. Quinone oxime present in the motor fuel by methods of production that will follow from reactions given above, or introduced into the motor fuel for that particular purpose may be treated with nitrogen trioxide, preferably in ethereal solution to yield corresponding diazo salts. Also by the action of chlorine or bromine on the phenyl hydrazine derivatives produced in any of the methods set forth above will result in the production of diazo salts.

The reactions referred to above have particularly emphasized the production of the diazo salts and compounds of the aromatic and cyclic type, whereas examples of producing the diazo paraffins have also been given at an earlier portion of this specification. The hydrazines may also be utilized for producing diazo paraffins. Thus alkyl hydrazines produced in the motor fuel by any of the methods set forth above on treatment with potassium pyrosulphate, followed by oxidation of the resulting compound with mercuric oxide yields diazo compounds. Thus ethyl hydrazine treated with potassium hydrosulphate gives potassium ethyl hydrazine sulphonate, $C_2H_5NH-NHSO_3K$, which on treatment with the mercuric oxide is converted into potassium diazo ethyl sulphonate $C_2H_5N=N.SO_3K$.

The importance of the diazo compounds is readily recognized because of their various reactivities to produce different types of derivatives of great importance in the modified motor fuels. Their reduction to produce hydrazines has already been indicated above, and such hydrazines are readily methylated or alkylated as by the treatment with methyl iodide to produce alkyl hydrazine. The reduction of the diazonium salts to the hydrazines may, for example, be carried out by treatment with stannous chloride and hydrochloric acid, the aqueous phase being agitated with the hydrocarbon phase containing the diazo salts until the desired reduction is produced.

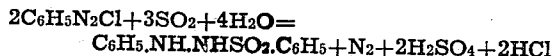
To briefly indicate some of the other important reactions of the diazo compounds, the following may be noted. If a motor fuel containing the diazo compounds are heated with absolute alco-

hol, they yield hydrocarbons and aldehydes. Thus phenyl diazonium chloride heated with absolute alcohol yields benzene on the one hand, and acetaldehyde on the other in accordance with the following equation:



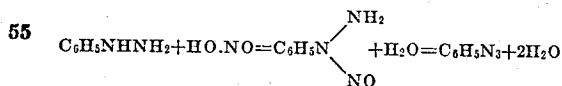
And by such reactions aldehydes may be readily produced in the motor fuel. If the motor fuel containing the diazo compounds are warmed and agitated with an aqueous solution, they yield phenols. Similarly warmed with halogen acids, halogen derivatives are obtained. Phenyl diazonium sulphate thus warmed with hydriodic acid yielding iodobenzene, nitrogen and acids. The various cuprous salts may be utilized in accordance with the Sandmeyer reaction to produce corresponding derivatives. Thus cuprous cyanide yields phenyl nitrile C_6H_5CN , and the nitriles, of course, upon reduction may be readily converted into amines. It is not intended by these reactions to indicate that specific individual compounds are being treated, but these reactions exemplify the complex derivatives that are producible in the motor fuels by these various treatments of the diazo compounds, complex mixtures of such derivatives, of course, being obtained by these treatments, since the motor fuels contain various diazo derivatives of complex character.

The diazo compounds treated with hydroxyl amine result in amines. Thus diazo benzene chloride yields aniline. And when treated with sulphur dioxide sulphazides are produced of which the following formulation is sufficiently exemplary:

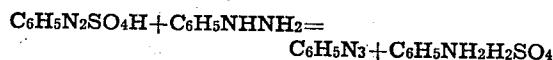


Such reactions may be carried out by agitating the hydrocarbon fractions containing the diazo compounds with aqueous solutions of sulphur dioxide, the water removing the acids present.

It may be noted that the aryl hydrazines when treated with nitrous acid yield nitrosyl derivatives, and the latter upon agitation with water are converted into azide derivatives. Such reactions may be carried out by agitating the hydrocarbon fraction containing the phenylhydrazine with the aqueous medium containing the nitrous acid, the process proceeding in accordance with the following reaction:



However, it may be noted that where the aryl hydrazines are present in the same composition with the aryl diazonium salts, the aryl azides will be produced by reaction between such components, one such reaction being formulated as exemplary between phenyl hydrazine and phenyl diazonium sulphate, as follows:

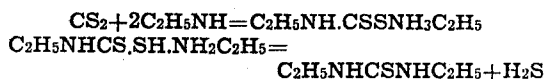


Thus the azides may be derived through the diazonium compounds, and the hydrazines, as well as through the Grignard reagents, as stated earlier.

While the processes set forth above show the production of various antioxidants, anti-gumming agents, etc. from constituents of the motor fuels themselves, the presence of various derivatives

therein, such as the amines, hydrazines, etc. lend themselves to the production of other types of anti-gumming constituents. Thus the semi-carbazides may be produced from the hydrazine derivatives present by treatment with potassium cyanide, the alkaline hydrazine sulphates being heated with the potassium cyanide for this purpose. Or the alkyl hydrazines treated with isocyanic acid or its esters results in the secondary NH— group receiving the carbamide residue.

If the motor fuel fractions containing primary or secondary amines are heated with carbon disulphide, preferably in alcoholic solution, or in the presence of alcohols formed in the motor fuels themselves, the resulting products heated to 110° yield dialkylated thioureas, the reactions being formulated as follows:



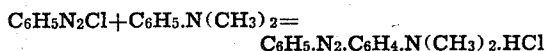
Urea derivatives may be produced by reaction of the aminized motor fuel fractions with phosgene or carbonyl chloride. Thus the aminized fractions if it is desired to convert primary amines therein into the urea derivatives are desirably treated with carbonyl chloride at temperatures of 260–270° C., but the secondary amines are more readily converted into the urea derivatives by action of the carbonyl chloride, or phosgene on the secondary amines in solution in the aminized motor fuel fractions.

Other types of anti-gumming derivatives, such as anthraquinone, are readily produced in the motor fuels containing aromatics by the addition of phthalic anhydride and aluminum chloride, the phthalic anhydride reacting with the benzol, for example, to give anthraquinone, while higher derivatives are produced from other homologues.

The various processes outlined above may be carried out by utilizing the reacting ingredients in their theoretical molecular equivalent proportions in accordance with the equations for the reactions illustrated. Such molecular equivalent proportions being based on the content of the ingredient of the motor fuel which is to be utilized. Thus where chlorhydrocarbons are being reacted, the reactions may be based on the use of the fraction containing the chlorhydrocarbons, utilizing an amount of such fraction which will yield the molecularly equivalent amount of chlorine. Similar considerations will apply to other reactions involving the amines, etc.

The presence of various derivatives of the diazo and amino types produced in the motor fuel fractions is set forth above, and other derivatives, such as the phenols, etc. lend such fractions desirably to the production of dyes in the motor fuels themselves.

Thus amino-azo compounds may be produced by reaction of the diazonium salts with aromatic amines and their derivatives, phenyl diazonium chloride yielding, for example, with dimethylaniline, dimethylaniline azobenzene in accordance with the following formulation:



This is exemplary of a wide variety of amino-azo compounds that can thus be produced directly in the motor fuel. Of course, individual compounds are thus not generally produced, since the diazonium compounds present in the motor

fuel by reactions as set forth above will be complex mixtures of such derivatives, and the result will be a heterogeneous mixture of derivatives; but the fluxing action of such derivatives with each other enables a homogeneous composition to be produced since only small portions of the dye need be necessarily present in any event to give the gasoline the desired color. Such derivatives may be produced by preparing the diazo compounds in the motor fuels themselves from constituents thereof, and adding the amines to react therewith from extraneous sources, or the aromatic amines may be produced in the motor fuel, and the diazo salts produced extraneously thereof, or both sets of compounds may be produced directly in the motor fuel from components thereof, and the dye developed in situ in the motor fuel.

In a strictly analogous manner, the diazo compounds may be coupled with phenols, amino phenols, etc., amino sulphonic acids and other derivatives usually coupled with such derivatives to produce amino azo compounds, or their derivatives.

Of course, such amino-azo derivatives may be further diazotized in the motor fuel, and coupled with further components to produce disazo dyes. As exemplary thereof, the following may be noted. A motor fuel fraction containing alpha-naphthylamine is coupled with diazotized para-anisidine using approximately a fraction of the motor fuel containing 30 parts of alpha-naphthylamine with approximately 25 parts of the diazotized compound. The resulting amino-azo derivative in the motor fuel is further diazotized by agitation with an aqueous medium containing 11 parts of hydrochloric acid and 15 parts of sodium nitrite for 1 hour at 10° C. The aqueous phase is separated, and approximately 30 parts of beta-naphthol are added to the motor fuel fraction containing the diazo compounds, and coupling takes place. If desired, however, to accelerate the coupling, the fraction containing the beta-naphthol and the diazo derivative may be agitated with an aqueous medium containing approximately 9 parts of caustic soda, and approximately 20 parts of sodium carbonate in water, the temperature being maintained at about 5° C. A bluish red dye is thus produced in solution in the gasoline fraction, directly therein, at least in part produced from components of the motor fuel itself. Since the naphthylamine may be produced with the motor fuel itself, the beta-naphthol may be produced in another portion of the motor fuel by reactions indicated above, and even the para-anisidine may be produced from a fraction of treated motor fuel by processes indicated above. Various derivatives of this type may be produced, so that a wide variety of disazo dyes may thus be produced directly in the motor fuel itself from its components.

Or again, ortho-anisidine may be diazotized and coupled with beta-naphthol to produce ortho-anisidine-azo-beta-naphthol as a dye coloring the gasoline, and produced directly in the motor fuel by processes that will follow from those given above.

Dyes of the indophenol and indamine type may be readily produced in the motor fuel from components therein. The production of various amines and phenol derivatives from components of the motor fuels has been given above. Where the aromatic amines are present in the motor fuel, it may be subjected to oxidation to pro-

duce the indamines therein, or phenols may first be added to produce the indophenol derivatives on oxidation, or where phenols are present, amines may be added from an extraneous source, or different fractions of the motor fuels may be treated to produce amines in one fraction and phenols in the other, and such fractions then mixed and subjected to oxidation to produce the desired indophenol or indamine, as the case may be. Thus for motor fuel fractions containing para-amido-dimethyl aniline and α -naphthol, or nitrosodimethylaniline and α -naphthol upon oxidation an indophenol is obtained. The reactions may proceed at room temperatures, but elevated temperatures may be employed, as for example, above 100° F. in which event the reactions are desirably carried out under pressure in order to avoid loss of desirable lighter constituents from the motor fuel. And this observation, of course, applies to the various reactions hereinabove set forth where the elevated temperatures are employed, and wherein pressures are desirably maintained in order to avoid loss of desirable constituents in the motor fuel.

The phthalein dyes may be prepared, for example, from motor fuel fractions containing phenol desirably produced from constituents of the motor fuel in situ by methods set forth above, by condensation with phthalic anhydride, phenol itself thus yielding phenol phthalein. Other phthalein derivatives may be prepared in an analogous manner.

The anthraquinone types of dyes are particularly important in the motor fuels, and may be readily produced therein from components of the motor fuel itself. The production of anthraquinone derivatives in the motor fuel has been illustrated above produced from components of the motor fuel itself. Such anthraquinone derivatives may be nitrated, and subsequently reduced, utilizing the nitration and reduction reactions illustrated above to produce amino-anthraquinones which may then be coupled with the desirable ingredients, such as diazotized para-amino-toluene. In this way, for example, 1-methylamino-4-para-tolyl amino-anthraquinone may be produced yielding a blue dye coloring the gasoline blue.

The acridine dyestuffs may similarly be produced in the motor fuel in situ from components of the motor fuel itself. For example, the aryl amines produced in the motor fuel may be condensed with benzaldehyde from an extraneous source, or the benzaldehyde may be produced in the motor fuel from constituents thereof, and the aryl amines introduced for the condensation reaction, followed by treatment with hydrochloric acid to split off ammonia, the oxidation to produce the dye base.

Various other types of dyes may, of course, be produced by analogous reactions. It should also be kept in mind that many of the dyes, and particularly the complex amino and phenolic compounds are in themselves anti-gumming agents, so that they have double properties in the motor fuel in producing not only a colored motor fuel, but also tend to prevent the formation of gums.

While various individual processes and methods of producing particular types of compounds have been set forth above, combinations of those various methods may be employed to produce double substitutions and various derivatives of organic character. For example, instead of chlorinating or halogenating the motor fuel

fraction, the motor fuel fraction may be aminized by the various methods referred to above, and then halogenated to produce chloramino derivatives in the motor fuel of both alkyl and aryl character, and such chloramino derivatives may thereupon be utilized for any of the reactions set forth above, including conversion into metallo organic derivatives having amino compounds bound in the molecule containing the metallo ingredient, or the Grignard reagents may be produced from the halogen-amino derivatives, for example, and such Grignard reagents reacted in accordance with the methods set forth above. So that various combinations of the several processes set forth herein may be utilized. And as indicated in connection with several individual methods set forth above, one portion of the motor fuel may be subjected to one type of treatment for the production of a particular class of derivatives, while another portion is subjected to a different treatment, and the two fractions then combined to have present both types of derivatives, or successive operations of these methods may be carried out to produce both types of derivatives. Of course, it must be kept in mind that not only are complex mixtures of derivatives produced in all of these instances where the types of reaction products are produced in the motor fuels themselves, and that where exemplary reactions are given, they are merely exemplary of the type of compounds being produced, since a number of derivatives in that class or type of compound will be produced by these reactions when carried out in situ, but complex combinations will take place between various ingredients of the motor fuels themselves, where different organic derivatives are present.

Furthermore, while the methods set forth above have been particularly illustrated in connection with their application to motor fuel fractions, those methods may be applied to petroleum oils or distillates or fractions therefrom, whether cracked or uncracked, before the distillation or preparation of the motor fuel fractions themselves, so that advantage may be taken of the subsequent steps utilized in the production of the motor fuels themselves to complete the processes of producing particular classes of compounds, as set forth herein. This may be illustrated in a number of ways. A number of the methods set forth above require the application of heat to complete the reactions. Such compounds as require heat to complete the reactions, particularly where elevated temperatures are employed, and the hydrocarbon materials undergoing treatment are, therefore, desirably treated under pressure, these methods may be carried out by taking the hydrocarbon materials before distillation or other heat treatment to produce the motor fuel fractions, and incorporating the necessary reactants to produce the classes of compounds desired, so that upon the distillation or heat treatment to produce the motor fuel itself, the methods are carried out for producing simultaneously the classes of compounds resulting from the reactions set forth. Similarly, a number of reactions as set forth above utilize reduction processes. In view of the wide use of hydrogenation methods in the production of motor fuels today, as well as lubricants, etc., the reduction reactions may take place at the same time that the hydrogenation treatment is utilized for producing the hydrogenated motor fuels. For example, the ingredients necessary to produce the desired classes of compounds upon reduction may be present in

the hydrocarbon material before the hydrogenation treatment applied to the motor fuel, so that upon completion of the hydrogenation treatment, the reduction of the compounds present may be simultaneously carried out, the hydrogenated motor fuel derivatives being produced at the same time that the classes of compounds for anti-gum or other purposes are being produced in the motor fuel. Similarly, where refining treatments are employed, involving treatments with caustic soda or sulphuric acid or successive treatments of that character, and where, for example, an acid treatment is necessary in connection with the production of particular types of compounds in accordance with the methods set forth above, the ingredients necessary to produce the desired derivatives upon treatment of sulphuric acid may be introduced into the hydrocarbon materials before the application of the sulphuric acid treatment, for example, so that the refining with sulphuric acid is carried out simultaneously with the treatment with acid necessary to produce anti-gum or other types of derivatives. These several examples will illustrate the application of ordinary refining methods as they are carried out at the present time in the plant, and their utilization in producing particular types of derivatives in the modified motor fuels in accordance with the present methods, so that a single reaction of that character is sufficient to accomplish both ends.

While the invention has been particularly illustrated with motor fuel fractions such as gasoline, other hydrocarbon fractions and distillates may be similarly treated. For example, components, fractions or distillates of the character known as lubricating oils and generally any of the hydrocarbon fractions and distillates produced from petroleum derivatives having boiling points substantially higher than the motor fuel ranges, may be treated by any of the methods set forth above so that such modified lubricating oils or other hydrocarbon fractions or distillates may be modified in accordance with the various methods set

forth above to produce new types of products containing the desired derivatives either produced outside of such lubricating oil or other hydrocarbon fraction or distillate and subsequently added thereto, or more desirably produced in situ by the methods set forth above in such lubricating oils or other hydrocarbon fractions or distillates.

Having thus set forth my invention, I claim:

1. A liquid hydrocarbon motor fuel containing a minor proportion of a metallo organo diazo compound.

2. A liquid hydrocarbon motor fuel containing a minor proportion of a metallo organo diazo-amino compound.

3. A liquid hydrocarbon motor fuel containing a minor proportion of a metallo organo diazo salt.

4. The process of producing modified motor fuels which comprises treating a liquid hydrocarbon motor fuel to produce a metallo alkyl therein, and converting the latter at least in part to a metallo organo diazo derivative.

5. A liquid hydrocarbon motor fuel containing a minor proportion of a component selected from the group consisting of metallo organo diazo compounds, metallo organo diazo-amino compounds, and metallo organo diazo salts.

6. A liquid hydrocarbon motor fuel containing a minor proportion of a metallo organo diazo compound produced in situ from a component of the hydrocarbon motor fuel.

7. A liquid hydrocarbon motor fuel containing a minor proportion of a metallo organo diazo-amino compound produced in situ from a component of the hydrocarbon motor fuel.

8. The process of making modified motor fuels which comprises treating a liquid hydrocarbon motor fuel to produce a metallo alkyl therein, and converting the latter at least in part to a metallo organo diazo-amino compound.

SOL SHAPPIRO.