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2,331,158

MOTOR FUEL

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No Drawing. Application July 27, 1940, Serial No. 348,020

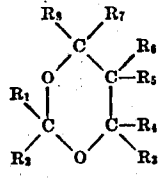
15 Claims. (Cl. 44—77)

The present invention relates to improved motor fuels of the gasoline type containing a meta-dioxane or a derivative thereof. The improved motor fuels of this invention may also contain other types of addition agents including anti-knock agents, such as metallo-organic compounds, (e. g., lead tetraethyl), alcohols, branched ethers, or other addition agents of this or of other types. This invention further relates to a method of processing low boiling, volatile naphthas which involves reacting the olefins in said low boiling naphtha with an aldehyde to form meta-dioxanes, thereby decreasing the overall volatility of said naphthas and also bringing about an improvement in their octane rating.

An object of this invention is to improve the octane numbers of gasoline motor fuels by incorporating therein a meta-dioxane or a derivative thereof. A further object of this invention is to decrease the volatility of volatile, low boiling naphthas, and also to increase the octane rating thereof. Another object of this invention is to provide a method of utilizing the olefins or individual types thereof present in said naphthas in the production of blending agents useful for improving the octane numbers of naphthas in which they are blended. Other objects and a fuller understanding of this invention may be had by referring to the following description and claims.

According to one phase of this invention, a meta-dioxane or a derivative thereof is blended with relatively low octane number motor fuels to improve the octane numbers of said fuels. Meta-dioxane and straight chain and branched chain hydrocarbon derivatives thereof are the blending agents which are of primary importance in carrying out this invention, although derivatives of the aforesaid meta-dioxanes, such as those containing oxygen and/or nitrogen in the side chains, are also of value as motor fuel blending agents.

The general structural formula for the compounds useful as blending agents according to this invention follows:

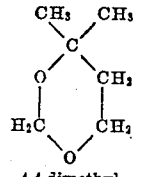


wherein R_1, R_2, R_3, R_4, R_5, R_6, R_7, and R_8 are hydrogen atoms or alkyl, aryl, aralkyl, alkaryl, alkenyl, alkinyl, and cyclo-aliphatic hydrocarbon radicals or substituted derivatives thereof, including alkoxy, alkoxyalkyl, acyl, aroyl, hydroxy, hydroxyalkyl, amino, aminoalkyl, ketoalkyl, amino hydroxy, aryloxy, carboalkoxy derivatives, and derivatives containing combinations of these substituents; R_5 or R_6 and R_7 or R_8 may also indicate the attachment of the respective ends of a chain of carbon atoms or of carbon and oxygen atoms at these positions, so that the meta-dioxane ring may be considered as having a fused-ring substituent, which may also contain hydrocarbon and/or hetero substituents of the types enumerated above.

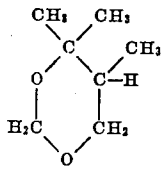
The meta-dioxanes and derivatives thereof may be suitably prepared by condensing the appropriate ethylenic derivatives with the appropriate aldehydes. By selecting the correct ethylenic derivative and the correct aldehyde, meta-dioxanes or derivatives thereof of any desired boiling point and octane rating can be obtained. Blending agents for the lower boiling gasolines or the higher boiling safety fuels can thus be prepared. The details of the method of preparation are fully disclosed and claimed in the application of John J. Ritter, Serial No. 334,668, filed May 11, 1940. In general, olefins, diolefins, or derivatives thereof, which may be present in admixture with paraffinic compounds, are condensed with aldehydes in the presence of aqueous solutions of acids or acid-acting compounds. Various conditions of temperature and pressure may be used in effecting the condensation, but temperatures in a range from atmospheric to 150° C. and pressures in the range from the vapor pressure of the reaction mixture to several atmospheres are generally sufficient. The length of time required for completing the reaction depends on the nature of the reactants and on the catalyst activity, but generally ranges from less than one hour to 10–12 hours. After completion of the condensation reactions, the reaction mixtures are neutralized, and the pure meta-dioxane or derivative thereof may be recovered therefrom by distillation.

Examples of catalysts which may be used in effecting condensation reactions of the above type are sulfuric, phosphoric, hydrochloric, fluoboric acids, boron fluoride, various organic acids, and aluminum sulfate and similar acid-acting salts, preferably in aqueous solution. Some of the meta-dioxanes and substituted derivatives thereof which may be prepared by the condensation of olefins or substituted derivatives thereof with aldehydes are 4,4-dimethyl meta-dioxane, prepared by the condensation of iso-

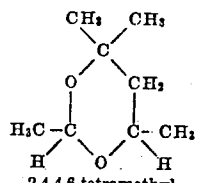
butylene with formaldehyde, 4,4,5-trimethyl meta-dioxane, prepared by the condensation of trimethylethylene with formaldehyde, 2,4,4,6-tetramethyl meta-dioxane, prepared by the condensation of isobutylene with acetaldehyde, 2,4,4,5,6-pentamethyl meta-dioxane, prepared by the condensation of trimethylethylene with acetaldehyde, 2,6-diphenyl-4,4-dimethyl meta-dioxane, prepared by the condensation of isobutylene with benzaldehyde, 4,4-dimethyl-5-ethoxymethyl meta-dioxane, prepared by the condensation of dimethallyl ethyl ether with formaldehyde, and 4,5-cyclohexo meta-dioxane, prepared by the condensation of cyclohexene with formaldehyde. The structural formulae for these compounds are presented below:



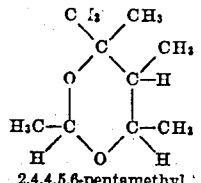
4,4-dimethyl meta-dioxane



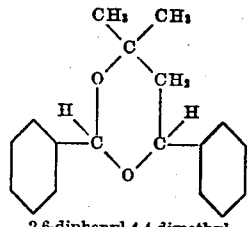
4,4,5-trimethyl meta-dioxane



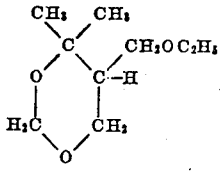
2,4,4,6-tetramethyl meta-dioxane



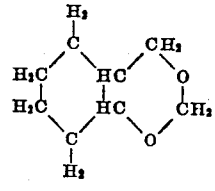
2,4,4,5,6-pentamethyl meta-dioxane



2,6-diphenyl-4,4-dimethyl meta-dioxane

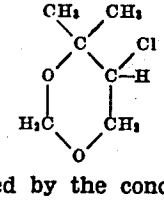


4,4-dimethyl 5-ethoxy-methyl meta-dioxane



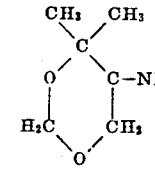
4,5-cyclohexo meta-dioxane

Others of the substituted meta-dioxanes can readily be prepared from the appropriate unsaturated compound and aldehydes or from halogen-containing meta-dioxanes. The latter are prepared by the condensation of halogen-containing olefin derivatives with aldehydes. For example, 4,4-dimethyl-5-chloro meta-dioxane.

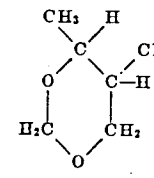


may be prepared by the condensation of isocrotyl chloride with formaldehyde. This compound and similar compounds may be converted into the corresponding hydroxyl derivative by hydrolysis, into the corresponding primary amine derivative by treatment with ammonia, into the corresponding secondary and tertiary amines by treatment with appropriate amines. The aforesaid hydroxyl derivatives may also be esterified, oxidized, etherified, etc. Other halogen-containing olefin derivatives, such as vinyl chloride, allyl chloride, dimethallyl chloride, isobutenyl chloride, etc., may be condensed with aldehydes to form halogen-containing meta-dioxanes which may be further reacted to form useful gasoline blending agents.

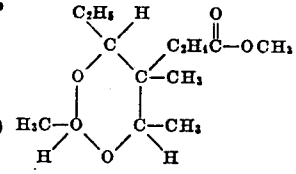
Structural formulae of several of these and other derivatives of meta-dioxanes which are useful as blending agents in motor fuels and which may be prepared by various methods are shown below:



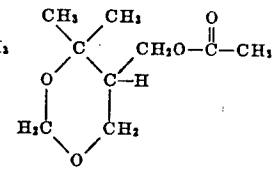
4,4-dimethyl-5-amino meta-dioxane



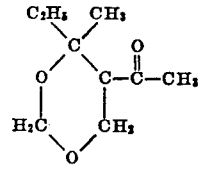
4-methyl-5-propoxy methyl meta-dioxane



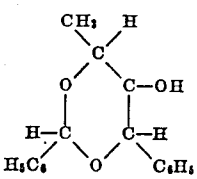
2,5,6-trimethyl-4-ethyl-5-carbomethoxy ethyl meta-dioxane



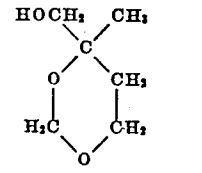
4,4-dimethyl-5-aceto oxymethyl meta-dioxane



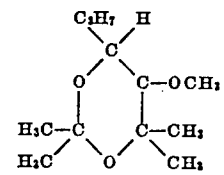
4-methyl-4-ethyl-5-aceto meta-dioxane



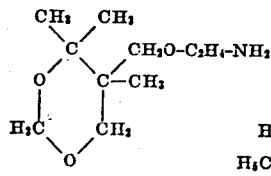
2,6-diphenyl-4-methyl-5-hydroxy meta-dioxane



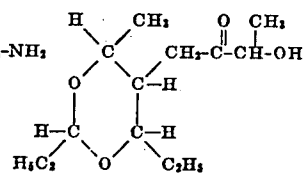
4-methyl-4-hydroxy-methyl meta-dioxane



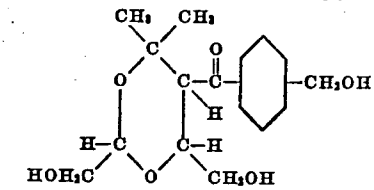
2,2,6,6-tetramethyl-4-isopropyl-5-methoxy meta-dioxane



4,4,5-trimethyl-5-amino-ethoxy methyl meta-dioxane



2,6-diethyl-4-methyl-5-(methyl hydroxyacetomethyl) meta-dioxane



2,6-di(hydroxymethyl) 4,4-dimethyl-5-(p-hydroxymethylbenzoyl) meta-dioxane

Instead of isolating the pure meta-dioxane or derivatives thereof from the olefin-aldehyde reaction mixture and blending the pure compound with motor fuel, the entire reaction mixture, after completion of the reaction and neutralization, may be added to motor fuel; the by-product dihydric alcohol, which constitutes 5–15% of the reaction mixture, forms a separate layer which may be separated from the motor fuel; thus, the final motor fuel blend contains the petroleum naphtha, a meta-dioxane, and a secondary or tertiary alcohol which is formed in small amounts in the olefin-aldehyde condensation reaction.

The meta-dioxanes or substituted derivatives

thereof, whether pure or used in conjunction with other addition agents, may be blended with motor fuels in any proportion. However, it is preferred to use the blending agents of this invention in amounts ranging from 5–50% of the motor fuel. As is pointed out above, other addition agents, such as anti-knock agents, e. g., lead tetraethyl and isopropyl ether, gum inhibitors, dyes, etc., may also be incorporated in motor fuels containing meta-dioxane blending agents.

Another phase of this invention is concerned with the generation of meta-dioxanes or substituted derivatives thereof in petroleum naphtha fractions, the resulting blends being of value as motor fuel. By the reaction of the olefins in a naphtha fraction with an aldehyde, such as formaldehyde or acetaldehyde, meta-dioxanes are produced in situ. The resulting compositions have higher octane numbers and higher octane blending values than do the starting naphtha fractions. Thus, treatment of an olefin-containing naphtha fraction with an aldehyde, in the presence of an acid-acting catalyst, is an effective method for increasing the octane number of the naphtha fraction.

Another advantage of this method of treatment accrues from the fact that several low-boiling hydrocarbon fractions available at petroleum refineries are unsuitable for use in motor fuels of the gasoline type because of their high volatility. Such fractions may be obtained from the products of cracking, reforming, or other operations carried out on petroleum materials at refineries. Treatment of such fractions with an aldehyde, such as formaldehyde, in the presence of a catalyst, such as aqueous sulfuric acid, results in the formation of a composition, the volatility of which is materially less than that of the starting naphtha fraction.

In carrying out the process discussed above, a low boiling naphtha fraction, such as a C_4 cut, is treated with an aldehyde, such as formaldehyde, in the presence of a catalyst. The resulting material is neutralized, and the aqueous neutralized catalyst-dihydric alcohol layer is separated. The remaining material, consisting of naphtha, a meta-dioxane, and a secondary and/or tertiary alcohol (depending on the olefins present in the naphtha), may be used as a motor fuel or as a motor fuel blending agent.

Variations in the latter procedure for obtaining high octane number motor fuel blends are possible. Thus, the reaction conditions may be such that the tertiary olefins, which are the most reactive type of olefins in a naphtha fraction, are reacted selectively with an aldehyde in the presence of a catalyst. This result can be achieved by carrying out such reactions under mild reaction conditions, that is, in the presence of quite dilute catalysts and at atmospheric temperature. If desired, the secondary olefins may be removed from the naphtha-tertiary meta-dioxane blend by suitable methods, and used for the synthesis of other chemical products.

Or, as an alternative, the tertiary olefins in a naphtha fraction may be selectively removed therefrom by treating the naphtha fraction with a sulfuric acid catalyst according to the "cold acid" process. The tertiary olefins are thereby polymerized to dimers, trimers, and tetramers, which can be readily separated by known means from the naphtha fraction. These polymers can subsequently be converted to the monomers by subjecting them to depolymerization conditions. The naphtha fraction, freed of tertiary olefins, may now be reacted with an aldehyde in the presence of a catalyst under such conditions that the primary and secondary olefins remaining therein react with the aldehyde to form meta-dioxanes. In general, the first of these variations gives more satisfactory results, since the tertiary meta-dioxanes have been found to have higher octane numbers than those of the primary or secondary meta-dioxanes. However, in the latter case, the tertiary olefin polymers, as such or after hydrogenation, may be blended back with the motor fuel blend containing the primary and/or secondary meta-dioxanes, or with other naphtha fractions. These polymers and hydropolymers have high octane numbers; in addition, the conversion of low boiling tertiary olefins into polymers boiling in the motor fuel range and the blending of said polymers with naphtha fractions affords another method for decreasing the volatility of low boiling naphtha fractions. Further, the tertiary olefins present in any naphtha fraction may be selectively polymerized or copolymerized with the olefins of other types present in said fraction, and the polymers may then be reacted in the naphtha or after separation therefrom with an aldehyde or aldehydes to form relatively high boiling meta-dioxanes, suitable for blending with safety fuels.

The following examples illustrate the invention:

EXAMPLE 1

A series of meta-dioxanes, namely, 4,4-dimethyl meta-dioxane, 4,4,5-trimethyl meta-dioxane, 2,4,4,6 - tetramethyl meta - dioxane, 2,4,4,5,6-pentamethyl meta-dioxane, prepared by the condensation of the appropriate olefin with formaldehyde or acetaldehyde in the presence of aqueous sulfuric acid catalysts, were blended with a reference motor fuel and the octane blending values of the meta-dioxanes were determined. The results of the several determinations are summarized in the following table:

TABLE 1

Meta-dioxanes as blending agents

Meta-dioxane	Boiling point, °C.	O. N. ref. fuel	Composition of blend		A. S. T. M. O. N. (clear)	Octane blending value of meta-dioxane	O. N. (3 cc. Pb)	Octane blending value (leaded) of meta-diaxone
			Per cent ref. fuel	Per cent meta-dioxane				
4,4-dimethyl meta-dioxane	131.5	65	75.6	24.4	73.1	98.2		
Do	131.5	65	50	50	83.3	102	91.5	102
Do	131.5	65	90	10	68.7	102	85.0	108
4,4,5-trimethyl meta-dioxane	152	65	75.6	24.4	72.0	93.7		
2,4,4,6-tetramethyl meta-dioxane	139	65	75	25	74.3	102.3		
2,4,4,5,6-pentamethyl meta-dioxane	161	65	75	25	74.4	102.6		

EXAMPLE 2

As pointed out above, instead of adding a pure meta-dioxane to a motor fuel, an olefin-aldehyde reaction mixture containing a meta-dioxane and a secondary or tertiary alcohol may be blended with a motor fuel. The following experiment illustrates this latter procedure and the results that may be obtained thereby.

120 gms. of paraformaldehyde and 100 cc. of 25% sulfuric acid were placed in a bomb, and 400 cc. of isobutylene were added thereto. The bomb was capped and placed on a shaking machine. Shaking was carried out at room temperature until the reaction of the paraformaldehyde with the isobutlyene was complete. The excess of isobutylene was then bled off, and the reaction mixture (two layers) was neutralized with 40 cc. of 45% sodium hydroxide. The lower aqueous salt layer was separated, and the upper product layer was dried over potassium carbonate. As indicated by analysis, the composition of the condensation product was as follows:

	Gms.	Wt. per cent
4,4-dimethyl meta-dioxane	146.5	62.9
Tertiary butyl alcohol	50	21.4
3-methylbutanediol-1,3	36.5	15.7
	233.0	100.0

150 cc. of this reaction product were blended with 408 cc. of 65 octane number reference fuel. The by-product glycol separated from the blend and was removed. The percentage of the reaction product in the final blend was 24.4 vol. %. The composition of the paraformaldehyde-isobutylene reaction product present in the blend was as follows: 74.6 wt. % of 4,4-dimethyl meta-dioxane, and 25.4 wt. % of tertiary butyl alcohol. The A. S. T. M.-octane number of the blend was 74.4, indicating an octane blending value of 103.5 for the meta-dioxane-alcohol motor fuel blending agent.

EXAMPLE 3

The following experiment illustrates the procedure used in reacting a low boiling refinery naphtha cut with formaldehyde. 200 cc. of 52.5% sulfuric acid were placed in a copper-lined bomb and 150 gms. of paraformaldehyde were added thereto. The bomb was capped and placed in a dry ice-alcohol bath. 480 gms. of refinery C_4 cut were then distilled into the bomb, and the valve on the bomb was closed. The analysis of this refinery C_4 cut was as follows: 16.4% isobutylene, 25% butene-2, 1.6% butene-1, the remainder being butanes. The bomb was placed on a shaking machine, and shaking was continued at room temperature for 7 hours. The excess gas was then bled off. Following this, the bomb was opened, and the contents were neutralized with 45% sodium hydroxide. The neutralized mixture (2 layers) was steam distilled. The distillate (2 layers) was treated with potassium carbonate, and the upper layer was separated and dried over potassium carbonate. The dried product was fractionated, the following fractions being obtained:

	Weight percent
48–85° C	3.8
85–126° C	2.4
126–131° C	14.2
131–132° C	69.1
Tower hold-up	10.5

From the exit gas analysis (0% isobutylene, 22.7% total unsaturates) and the amount of the exit gas, it was determined that 2.3 mols of the C_4 olefins had reacted with formaldehyde. From the distillation data, it was determined that the split between the meta-dioxanes formed in this reaction was as follows: 61% of 4,4-dimethyl meta-dioxane (obtained from isobutylene) and 39% of 4,5-dimethyl meta-dioxane (obtained from butene-2). The yield of the meta-dioxanes, based on the olefins reacted, was 60 mol per cent.

From the composition of this reaction mixture and the octane number blending data presented in Example 1, it can readily be seen that the reaction mixture prepared in the present experiment would make a very satisfactory motor fuel or motor fuel blending agent.

The above disclosures and examples are given for the purpose of illustration only and are not to be construed as in any way limiting the invention.

What is claimed is:

1. A gasoline motor fuel comprising a hydrocarbon distillate boiling between 65–205° C. and a meta-dioxane boiling within the gasoline boiling range and chosen from the group consisting of meta-dioxane, meta-dioxanes bearing hydrocarbon substituents, meta-dioxanes bearing oxygen-containing substituents, and meta-dioxanes bearing nitrogen-containing substituents.

2. A gasoline motor fuel comprising a major proportion of a hydrocarbon distillate boiling between 65–205° C. and a minor proportion of a meta-dioxane boiling within the gasoline boiling range.

3. A gasoline motor fuel comprising at least 50% of a hydrocarbon distillate boiling between 65–205° C., and a meta-dioxane boiling within the gasoline boiling range.

4. A gasoline motor fuel comprising a major proportion of a hydrocarbon distillate boiling between 65–205° C. and a minor proportion of 4,4-dimethyl meta-dioxane.

5. A gasoline motor fuel comprising a major proportion of a hydrocarbon distillate boiling between 65–205° C. and a minor proportion of 2,4,4,5,6-pentamethyl meta-dioxane.

6. The method of producing an improved gasoline motor fuel which comprises contacting a refinery naphtha fraction with an aldehyde in the presence of a polybasic oxygenated mineral acid of 10–85% concentration with agitation, at a temperature of 15–40° C., at a pressure sufficient to maintain the reactants in the liquid phase, and for a length of time sufficient to complete the reaction between the unsaturated hydrocarbons present in the naphtha fraction and the aldehyde.

7. The method of producing an improved gasoline motor fuel which comprises contacting a refinery C_4 naphtha fraction with an aldehyde in the presence of sulfuric acid of 10–85% concentration with agitation at a temperature and pressure sufficient to maintain the reactants in the liquid phase and for a length of time sufficient to complete the reaction between the unsaturated hydrocarbons present in the naphtha and the aldehyde.

8. The method of producing an improved gasoline motor fuel which comprises contacting a refinery C_5 naphtha fraction with an aldehyde in the presence of sulfuric acid of 10–85% concentration with agitation at a temperature and pressure sufficient to maintain the reactants in the

liquid phase and for a length of time sufficient to complete the reaction between the unsaturated hydrocarbons present in the naphtha fraction and the aldehyde.

9. The method of producing an improved gasoline motor fuel which comprises contacting a refinery naphtha fraction with an aldehyde in the presence of sulfuric acid of 10–30% concentration with agitation at a temperature and pressure sufficient to maintain the reactants in the liquid phase and for a length of time sufficient to complete the reaction between the tertiary olefins present in the naphtha fraction and the aldehyde, the primary and secondary olefins being recovered from the reaction mixture and utilized in the synthesis of other products.

10. An improved gasoline motor fuel consisting of a hydrocarbon distillate boiling between 65–205° C., a lead alkyl, and 5–50% of a meta-dioxane.

11. An improved gasoline motor fuel consisting of a hydrocarbon distillate boiling between 65–205° C., a lead alkyl, and 5–50%, of 4,4-dimethyl meta-dioxane.

12. An improved gasoline motor fuel consisting of a hydrocarbon distillate boiling between 65–205° C., a lead alkyl, and 5–50% of 2,4,4,5,6-pentamethyl meta-dioxane.

13. An improved gasoline motor fuel consisting of a hydrocarbon distillate boiling between 65–205° C., lead tetraethyl, and 5–50% of a meta-dioxane.

14. An improved gasoline motor fuel consisting of a hydrocarbon distillate boiling between 65–205° C., lead tetraethyl, and 5–50% of 4,4-dimethyl meta-dioxane.

15. An improved gasoline motor fuel consisting of a hydrocarbon distillate boiling between 65–205° C., lead tetraethyl, and 5–50% of 2,4,4,5,6-pentamethyl meta-dioxane.

ERVING ARUNDALE.
LOUIS A. MIKESKA.