

## UNITED STATES PATENT OFFICE

2,275,175

## MOTOR FUEL

Gould H. Cloud, Linden, N. J., assignor to Standard Oil Development Company, a corporation of Delaware

No Drawing. Application November 30, 1939,  
Serial No. 306,841

## 5 Claims. (Cl. 44-9)

This invention relates to fuels adapted for high-compression spark-ignition engines. More specifically, it relates to blending agents which increase the utility and efficiency of such motor fuels.

In the past, the addition to gasoline in extremely small amounts of substances which function as gum inhibitors has been practiced. Such gum inhibiting substances have included amino and phenolic bodies which, in general, have only a slight solubility in the gasoline and, therefore, had to be used in extremely low concentrations, substantially below 1%, usually less than 0.5%, or even 0.1%. While the value of the known gum inhibiting agents has not been negated in their application for stabilizing ordinary refined gasolines by the limitations of their solubilities, their usefulness has been somewhat rigidly restricted in and to this stabilizing function.

In accordance with the present invention, it has been determined that from among the derivatives of phenol there are some which can serve in far greater capacity than the gum inhibitors for improving ordinary gasoline, and various other types of motor fuel compositions, also. These more versatile and beneficial phenolic derivatives are selected from the class of alkyl phenols characterized in common by compounds which are normally liquid and have low melting points. These compounds also have a substantial miscibility with gasoline hydrocarbons, being capable of forming blends therewith in concentrations amounting from about 2% to 10%, or more, by volume of the blend.

Among the objects and advantages of the present invention is the provision of motor fuel blends having significantly improved anti-knock values. A further object of this invention is to provide motor fuels of high stability and of consistently high anti-knock value, even when containing large proportions of cyclic and unsaturated hydrocarbons and used in engines run at high temperatures. These and other objects will become more apparent from the following description.

While an examination of the physical properties of the known phenol derivatives indicates that relatively few possess properties which enable them to be suitable for the purpose of the present invention, the normally liquid alkyl phenols which have been tried demonstrate that they make very valuable and unexpected improvements in a motor fuel.

To attain the objects of this invention, a nor-

mally liquid alkyl phenol of satisfactory low melting point is preferably added in a minor proportion, yet in substantial amounts effective for improving the anti-knock value of a motor fuel having a hydrocarbon fuel base.

Among the best normally liquid alkyl phenols for the purpose in hand is the compound meta-isopropyl-ortho-cresol, commonly termed carvacrol. The classical method for obtaining this compound is by heating camphor with iodine. It has a boiling point of about 458° F., which comes within the range of boiling points for gasoline hydrocarbons. It has a melting point of 33° F., which is sufficiently low to avoid the practical objection to phenolic bodies that are crystalline at ordinary temperatures and thus would tend to plug the carburetor jets of engines, if present in large percentages in the motor fuel. To illustrate how the normally liquid alkyl phenols, such as carvacrol, can be blended in large proportions with commercial gasolines to enhance the anti-knock value of these fuels, a 10% blend of carvacrol in a standardized reference fuel having an A. S. T. M. octane number of 65 showed an A. S. T. M. octane number of 78.5. Thus, an improvement of 13.5 cetane numbers was obtained by the addition of this alkyl phenol blending agent, indicating that it has an octane blending value of the order of 200.

Although carvacrol is one of the most effective low melting point alkyl phenols for increasing the anti-knock value, others possess satisfactorily high blending values of at least about 100. As a general rule, it has been observed that the alkyl substituents in the low melting point phenols contain from 2 to about 7 carbon atoms per molecule; that in the monoalkyl phenols, the alkyl group is preferentially in the ortho or meta position with respect to the hydroxy group, and that the dialkyl phenols are suitable when a lower alkyl group, such as a methyl or ethyl group, is similarly in the ortho or meta position with respect to the hydroxy group, the other alkyl group being branched, containing 3 to 5 carbon atoms, and being in a position meta or para to the hydroxy group.

A number of the suitable low melting point alkyl phenols comparable to carvacrol may be prepared cheaply by alkylating ortho and meta cresols with secondary or tertiary alkylating agents such as iso-olefins or iso-alkane halides under known alkylating conditions which may involve intervention by known alkylating catalysts, for example, anhydrous metal halides,

sulfuric acid, phosphoric acid, or activating clays. The branched aliphatic alkylating agents are readily obtainable from refinery gases containing propene, butenes, and amylenes.

Alkyl halides are the most common alkylating agents because they are produced at low cost and can be condensed readily with phenol and its homologues. Branched alkyl halides react with sufficient ease to alkylate without the intervention of a catalyst. But even with these alkylating agents a catalyst hastens the reaction. Alkylation by olefins is usually carried out in the presence of a sulfuric acid or phosphoric acid catalyst, and in the alkylation by straight chain olefins having at least 3 carbon atoms per molecule there is a tendency for the olefin to rearrange and introduce an iso-alkyl substituent into the phenol. Another type of alkylating agent comprises di-alkyl sulfates which are caused to react with the phenolic compound in the presence of an alkali.

The preparation of carvacrol and analogous iso-alkyl cresols is satisfactorily effected by reacting ortho-cresol with the desired iso-alkyl halide. The reaction occurs very readily at low temperatures such as at  $-10^{\circ}\text{C}$ . or lower.

A further valuable property exhibited by the normally liquid alkyl phenols in improving the efficiency and utility of motor fuels is their ability to reduce what is known as high temperature depreciation or "fade" in octane number of motor fuels. It has been found that the use of aromatic hydrocarbons, olefinic hydrocarbons, and other easily oxidizable high octane number fuel ingredients, is restricted greatly by the fact that these compounds tend to lower the octane number of the fuel when it is used in an engine run at high temperatures, such as encountered in the operation of air-cooled aviation motors.

The improvement made by a normally liquid alkyl phenol in reducing the high temperature depreciation of octane number was evaluated by testing a blend of 25% toluene in a 65 A. S. T. M. octane number gasoline reference fuel in an engine subjected to widely varying temperatures. The deviation in octane number was found to be as much as 3.8 octane numbers. It was observed that when 2% of the normally liquid alkyl phenol was blended with this same composition and tested in an engine over the same temperature range, the blend showed an A. S. T. M. octane number increase of 2.6 and a deviation of only 2 octane numbers. Accordingly, the octane number depreciation or fade was reduced by about 48%.

Specific examples of normally liquid alkyl phenols which may be used to impart benefits to a fuel similar to those obtained by the addition of carvacrol (meta-isopropyl-ortho-methyl phenol) are meta- and ortho-ethyl phenols, para-tert-butyl meta- and ortho-cresols, ortho-tert-amyl phenol, para-isobutyl meta- and ortho-cresols, meta-isopropyl-meta-ethyl phenol, para-isopropyl-ortho-ethyl phenol, ortho-isoamyl phenol, and others of these types having melting points below  $50^{\circ}\text{F}$ ., and preferably below  $40^{\circ}\text{F}$ .

The action of the normally liquid alkyl phenols in maintaining the octane number of a fuel more consistent through changes in motor operative conditions rate the effect of these blending agents on the octane number of the fuels varies with the concentration of the agents in the fuel. Accordingly, while an appreciable improvement is obtained when these blending agents are added

to a fuel in concentrations of from 1% to 2% by volume, a more substantial and preferred improvement is obtained when the concentration is more than 1% and, more particularly, from about 2% to 15%.

Substantially all the low melting point alkyl phenol blending agents of the types mentioned have boiling points in the range of  $395^{\circ}\text{F}$ . to about  $475^{\circ}\text{F}$ .; therefore, they have volatilities corresponding to those of gasoline hydrocarbons found in the heavy ends of commercial gasolines. This volatility characteristic is advantageous in the use of the low melting point alkyl phenols for raising the anti-knock properties in the heavy ends of gasoline fuels and for improving high flash points of safety fuels fractionated to have boiling ranges within the limits of  $300^{\circ}\text{F}$ . to  $475^{\circ}\text{F}$ ., or to  $600^{\circ}\text{F}$ .

The low melting point alkyl phenols contemplated by this invention form stable blends with hydrocarbon motor fuels in proportions ranging from 2% to 15%, and sometimes higher. They are difficultly soluble in water; hence, they are not readily removed from the fuel upon addition of moisture. Fuel compositions containing these phenols are highly stable to oxidation, even when they contain much larger proportions of unsaturated and aromatic hydrocarbon compounds than are present in ordinary commercial gasolines, e. g. proportions above 20% by volume of the fuel composition. The dialkyl phenols, such as isoalkyl cresols and isoalkyl ethyl phenols have been observed to exhibit a marked ability to stabilize the color of gasoline hydrocarbons. They show a definitely noticeable effect in retarding the formation of color in a colorless or white gasoline exposed to sunlight even when added to the gasoline in concentrations as low as about 0.01%. In the increased concentrations in which they are capable of being used, they prevent discoloration of a gasoline motor fuel over long periods.

With the described low melting point alkyl phenol blending agents used individually or in mixtures, other additives for improving the fuels may be used, for example, lubricants, gum fluxes, dyes, thickeners, corrosion inhibitors, etc. The hydrocarbon base of the fuel is selected according to the requirements of the engine. For a carburetor type engine, the base fuels may be any of the usual types of commercial gasolines having boiling ranges within approximate limits of  $100^{\circ}\text{F}$ . to  $475^{\circ}\text{F}$ . For injection type spark-ignition engines, the base fuels may have a higher initial point, such as  $300^{\circ}\text{F}$ . and an end point approaching  $600^{\circ}\text{F}$ . The low melting point alkyl phenols used according to the present invention have boiling points which come well within such limits.

Many modifications and variations of the invention as hereinbefore set forth may be made without departing from the spirit and scope thereof. It is, therefore, intended that the invention should not be limited by the examples, nor by specifically described functions and uses of the blending agents which have been set forth for the purpose of illustration.

I claim:

1. A high compression spark-ignition motor fuel composed substantially of gasoline hydrocarbons in a major proportion blended with an octane number improving amount of 2 to 15% by volume of a dialkyl phenol wherein a methyl group is one of the positions ortho and meta to the hydroxy group, and a branched alkyl group

containing 3 to 5 carbon atoms, para to the hydroxy group, said dialkyl phenol having a melting point below 40° F. and a boiling point within the range of about 395° F. to 475° F.

2. A composition as described in claim 1 in which the dialkyl phenol is an iso-alkyl ortho-cresol.

3. A high compression spark-ignition motor fuel substantially composed of gasoline hydrocarbons in a major proportion blended with an octane number improving amount of from 2% to 10% by volume to a dialkyl phenol, having one alkyl group of 1 to 2 carbon atoms ortho to the hydroxy group, and an isoalkyl group of from 3 to 5 carbon atoms meta to the hydroxy group, said dialkyl phenol having a melting point below 40° F. and a boiling point within the approximate limits of 395° F. to 475° F.

4. An anti-knock motor fuel for high compression spark-ignition engines, substantially composed of gasoline hydrocarbons blended with 2 to 10% by volume of meta-isopropyl-ortho-methyl phenol.

5. An anti-knock motor fuel for high compression spark-ignition engines, substantially composed of a hydrocarbon fuel boiling in the range of 100° F. to 600° F. blended with 2% to 15% by volume of a dialkyl phenol wherein an ethyl group is in one of the positions ortho and meta to the hydroxy group and a branched alkyl group containing from 3 to 5 carbon atoms in the meta position with respect to the hydroxy group, said dialkyl phenol having a melting point below 40° F. and a boiling point within the boiling range of said hydrocarbon fuel.

GOULD H. CLOUD.