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HIGH-COMPRESSION MOTOR FUEL

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This invention relates to the production of motor fuels, especially aviation gasolines, having unusual anti-detonating properties as well as stability against separation of solid material at very low temperatures.

It is well known that a gasoline of low anti-knock value may be improved by the addition of a knock-suppressing additive such as tetraethyl lead, or by modification of its composition, for example, by cracking it to increase its content of aromatic-type and/or olefinic-type hydrocarbons, or by adding these hydrocarbons to the gasoline. In attempting to produce gasolines of relatively high anti-knock quality by combining these effects, however, i. e., by the use of both tetraethyl lead and olefinic and/or aromatic-type hydrocarbons, it has generally been found that the presence of such hydrocarbons reduces the effectiveness of the tetraethyl lead markedly, so that gasolines containing moderate amounts of both tetraethyl lead and olefinic and/or aromatic hydrocarbons, for example, may even be of no better anti-knock rating than a similar gasoline containing the same amount of tetraethyl lead, but no olefins or aromatics.

Primary aromatic amines such as aniline are also known to increase gasoline anti-knock rating, particularly when the gasoline is of relatively low anti-knock quality and contains no additives such as tetraethyl lead. Such amines behave as super-aromatics in that they are generally many times as effective as the corresponding aromatics, but the prior art shows that they frequently have similarly harmful effects on lead susceptibility, or response to the addition of tetraethyl lead, and therefore have been considered of little value for use in gasolines of high anti-knock rating containing moderate to large amounts of tetraethyl lead. For example, it is shown in U. S. Patent No. 2,230,844 that when 2% of various primary amines were added to an aviation gasoline containing no tetraethyl lead and having a C. F. R. motor method octane number of about 85, the octane number was increased in all cases by about 2 to 7 points; whereas when the same amounts of the same amines were added to the same gasoline containing 2 ml. of tetraethyl lead per gallon and having an octane number of about 97, the octane number was actually reduced in most instances, the reduction amounting to nearly 2 points in three of the eight examples shown.

I have discovered that contrary to expectations based on the above described earlier observations, the addition of small amounts of primary aromatic amines to aviation-type gasolines of extremely high anti-knock value and containing relatively large amounts of tetraethyl lead has definitely beneficial effects on their anti-knock characteristics. Furthermore, even more unexpected improvements in anti-knock quality may be realized by the inclusion of aromatic hydrocarbons in the amine-containing blend, provided that the aromatics are present in at least a critical minimum concentration. Secondary aromatic amines have also been found to exhibit the same phenomena as the primary aromatic amines. It has further been discovered that the presence of both aromatic amines and aromatic hydrocarbons in the same gasoline has another beneficial effect, i. e., the aromatic hydrocarbons tend to lower the "compatibility temperature" of the gasoline, as brought out below.

Since motor gasolines may be used at extremely low temperatures, as in arctic climates or at stratospheric temperatures in the case of aviation gasolines, it is necessary that they remain homogeneous mobile liquids at these low temperatures as well as at normal atmospheric temperatures, to prevent plugging of lines, filters, etc., and to prevent loss of desirable ingredients. It has been found that many gasolines, on being subjected to low temperatures in the region of -50° F. to -100° F., will exhibit a lack of "compatibility," i. e., will show separation of substantial amounts of a second phase, usually a solid, sometimes crystalline in appearance. There is usually a fairly well defined temperature above which the gasoline will remain substantially homogeneous, but below which there may be a definite separation of a second phase, and this temperature is what is referred to herein as the "compatibility temperature." It has been discovered that gasolines containing certain amines, as well as those containing certain aromatics, and those containing certain combinations of amines and aromatics, have exceptionally low compatibility temperatures. It is an object of this invention therefore to provide motor fuels containing certain amines and having exceptionally low compatibility temperatures. It is another object of this invention to provide motor fuels containing certain amines and having exceptionally good anti-detonation characteristics as well as exceptionally low compatibility temperatures.

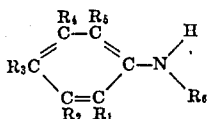
According to this invention, gasolines of good anti-detonation characteristics, containing substantial amounts of isoparaffinic hydrocarbons, as well as tetraethyl lead and aromatic amines, are improved both in increased anti-detonation

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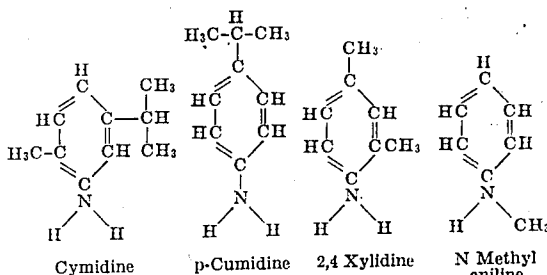
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characteristics and in lowered compatibility temperatures by the addition of aromatic hydrocarbons. The most suitable amines, aromatic hydrocarbons, gasoline blends, test methods, etc., are described in the following paragraphs.

The amines useful in this invention are those of the following type:



in which R₁ to R₆ inclusive are hydrogen or phenyl or saturated alkyl hydrocarbon groups. In order to provide for low compatibility temperatures as well as reasonable volatility, those amines containing at least 7 and preferably between about 7 and 12 carbon atoms are preferred. Among the most effective of these in improving the anti-knock quality of gasolines, are cumidines, cumidines, xylidines, and N methyl aniline. Formulas of the last named amine and of one isomer of each of the first three follow:



There are other isomers of the first three materials shown, which are also effective anti-knock blending agents. These isomers may vary considerably not only in their anti-knock effectiveness, but also in their effects on the compatibility temperature of the gasoline. For example, among the six possible xylidine isomers, the 3,4 xylidine has the most pronounced anti-knock effect, but is the least effective in maintaining low compatibility temperatures; while the mixture of isomers derived from m-xylene is in general excellent both in anti-knock effect and in effectiveness in maintaining low compatibility temperatures. It has also been observed that for aromatic amines having alkyl substituents containing 3 or more carbon atoms, the branched chain isomers are preferable. For example the cumidines are preferable to the n-propyl amino benzenes.

Mixtures of aromatic amines or amine isomers may be employed and are frequently more desirable, especially from a compatibility temperature standpoint, than a single isomer. A very effective material is a mixture of amines prepared by nitration of aromatic hydrocarbon concentrates followed by reduction of the product. In one instance such a concentrate was prepared by solvent extraction of a California crude gasoline fraction boiling in the range of about 270 to 360° F. This concentrate contained about 70% aromatic hydrocarbons having about 7 to 10 carbon atoms and about 30% of naphthenic and paraffinic hydrocarbons. In another instance an aromatic hydrocarbon concentrate was prepared by catalytic reforming of a 200° to 260° F. boiling range fraction from a California crude at a temperature of about 950° F. in the presence of about 5000 cubic feet of hydrogen per barrel of

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liquid feed, employing a molybdc oxide on alumina catalyst; separating from the product a xylene fraction boiling in the range of about 270° to 290° F. and containing about 82% aromatic hydrocarbons, preponderantly xylenes, and less than about 5% of olefins. Nitration of this fraction; followed by reduction of the product as described below, yielded a mixture of amines, predominantly xylidines, which was unusually effective both in improving anti-knock qualities and in maintaining low compatibility temperature.

The aromatic hydrocarbons to be used in conjunction with the above amines for the purposes of this invention, are in general those which have saturated alkyl side chains, and contain at least 7 carbon atoms, and preferably from 7 to about 10 carbon atoms in the molecule. These include toluene, the xylenes, mesitylene and other trimethyl benzenes, ethyl benzene, cymene, cumene, etc., or mixtures containing such hydrocarbons, such as aromatic hydrocarbon concentrates prepared by solvent extraction of naphtha. Aromatic hydrocarbon concentrates obtained from the products of certain types of cracking processes such as the catalytic hydroforming operation described above are also suitable in many instances, particularly if they contain no diolefins, less than about 0.05% sulfur, and a very low olefin content, such as less than about one-tenth the aromatic hydrocarbon content. The product described above is especially suitable for the purposes of this invention. Such products differ from typical cracked gasoline, since it is usually necessary to have hydrogen introduced into the catalytic reforming unit, and/or to treat the product with hydrogen, sulfuric acid, clays, etc., to remove excessive amounts of olefins and sulfur compounds, which must not be present in the gasolines of this invention.

In the aromatic hydrocarbons, as well as the amines, there is also a wide variation in the effectiveness of the various isomers. Among the three xylene isomers, for example, the meta- and para-isomers are most effective in enhancing the anti-knock qualities of the gasolines containing the aromatic amines, but the meta- and ortho-isomers, especially the meta-, are most effective in reducing the compatibility temperature of the gasoline. Also the aromatics having branched chain substituents are in general preferable to the corresponding aromatics having the substituent carbon atoms in a straight chain.

The motor fuels of this invention are those of any conventional type which have octane numbers by the well known A. S. T. M. or C. F. R. motor method of about 75 or above, and are therefore suitable for use in high compression internal combustion engines. The invention is particularly applicable to aviation gasolines having anti-detonation characteristics equal to or superior to those of pure isooctane (2,2,4-trimethyl pentane), such as for example, the 100 octane gasoline of commerce. It is desirable that these motor fuels be resistant to deterioration in storage under severe conditions, and this requirement not only prohibits the presence of more than traces of diolefins or any substantial amounts of olefins, as described above, but also frequently makes desirable the inclusion of a small amount of an antioxidant, such as the conventional amino-phenols, etc. These motor fuels must also have certain volatility characteristics, for example, a Reid (A. S. T. M. method D323-42), 75 vapor pressure between about 5 and 12 pounds

and preferably about 7 pounds, and an Engler distillation range of about 80° to about 450° F. and preferably about 100° to about 350° F. It is preferred that they contain an anti-detonant such as tetraethyl lead. The latter may be employed in substantial amounts, such as 1 to 10 ml. or more per gallon, preferably about 2 to 4 ml. per gallon. They generally contain large amounts of isoparaffinic material such as isopentane, isooctane, alkylate, etc. Their content of normal paraffins should be low, but there may be moderate amounts of naphthenes especially alkylated naphthenes, present as well as the aromatics described above. The anti-knock ratings of the preferred gasolines of 100+ octane number may be determined by the so-called AFD-3C rich mixture method described in U. S. Army-Navy Specification AN-VV-F-748a. This method utilizes commercial isooctane (S-2 reference fuel) containing tetraethyl lead as a basis for comparison, and the knock-rating is reported as the ml. of tetraethyl lead required to be added to the S-2 reference fuel to match the anti-knock quality of the gasoline in question.

Since, as mentioned above, it is desirable that the gasolines of this invention remain homogeneous at all times prior to actual vaporization and combustion, it is desirable that they have low compatibility temperatures, such as below about -50° F. and preferably below about -76° F. The compatibility temperature may be determined by chilling a 20 ml. sample of the gasoline contained in a vacuum jacketed test tube provided with a mercury-sealed stirrer and protected from atmospheric moisture by use of a calcium chloride filled drying tube, reducing the temperature at a rate of about 4° F. per minute until a temperature of -110° F. is attained, or a substantial separation of a second phase (usually a solid) takes place, then holding this minimum temperature constant for 20 minutes, and finally allowing the temperature to rise at a rate of about 1° F. per minute until substantially all of the second phase is redissolved. The mixture is stirred continuously throughout the test. The temperature at the point of substantially complete re-solution is taken as the compatibility temperature, since it has been found that super-cooling normally occurs before the separation of second phase occurs during the chilling.

It has been found possible to correlate this compatibility temperature, for the gasolines of this invention, in a general way although not rigorously, with the melting points of the added amines and aromatic hydrocarbons, higher melting points generally leading to higher compatibility temperatures. For example, blends containing meta-xylene and the amines derived therefrom have much lower compatibility temperatures than blends containing para-xylene and 3,4-xylylidine. This agrees with the melting point data, since 3,4-xylylidine has a melting point of +50° C., while the melting point of the mixed meta-xylylides is below -50° C.; and similarly para-xylene has a melting point of +13° C., while meta-xylene melts at -54° C. On the basis of solubility, therefore, those aromatic amines and aromatic hydrocarbons of this invention which have low melting points, such as below about -15° C., and preferably below about -50° C. are preferred. These may be separated from the less desirable materials of higher melting point by selective crystallization of the latter and recovery of the desired non-crystallized material by conventional methods.

In the preparation of the gasolines of this invention, the above described amines are used in concentration of about 0.5% to about 15% or more, preferably about 1% to 5%, in the finished gasolines, which are blended to conform to the above requirements. In order to obtain the enhanced anti-knock value of the amines in the presence of the aromatic hydrocarbons described, the latter must be present in a concentration greater than a critical minimum value of about 5%, and are preferably used in concentrations above about 9%. Percent as used herein refers to percent by liquid volume at room temperature.

As specific examples of the enhanced anti-detonation tendencies of gasolines containing the amines and aromatics specified in this invention, a series of basic aviation-type blends containing various amounts of aromatic-type hydrocarbons was prepared. These blends contained 22% of isopentane, 18% of California straight-run gasoline heart cut containing about 5% of aromatic-type hydrocarbons, and 60% of mixtures in various proportions of alkylate and the above-described aromatic hydrocarbon concentrate prepared by solvent extraction and containing about 70% of aromatics. Boiling ranges of the heart cut and alkylate were approximately 100° F. to 225° F. and 100° F. to 300° F. respectively, and the alkylate was obtained by a conventional alkylation of isobutane with butenes and pentenes in the presence of concentrated sulfuric acid. Four such blends were prepared by varying the proportions of alkylate and aromatic concentrate so as to obtain products containing 1, 5, 11, and 15% of aromatics respectively. These four contained no aniline, and a similar series of four was prepared with 3% of aniline added. All eight gasolines were leaded with 4.0 ml. tetraethyl lead per gallon and tested by the AFD-3C rich mixture method. The following knock rating data were obtained:

Aromatic hydrocarbon content, per cent	Knock rating, S-2 plus indicated ml. tetraethyl lead per gallon	
	No aniline added	3% aniline added
1.....	0.7	1.8
5.....	.6	1.7
9.....	.5	2.1
15.....	.4	2.9

These data show that aniline is effective in this fuel even in the absence of an appreciable quantity of aromatics, but that its effect is remarkably enhanced when the concentration of aromatics is over about 5%, and preferably over about 9%.

Other primary and secondary aromatic amines were similarly effective in blends similar to those above containing about 15% aromatics. For example 3% of commercial mixed xylylidine isomers (predominantly meta-xylene derivatives, with no ortho-xylene derivative) raised the knock rating from 0.4 to 2.4 ml.; 3% of cumidine isomers prepared from commercial cumene by nitration and reduction raised the knock rating from 0.4 to 2.0; 3% of the mixed products obtained from the above 70% aromatic hydrocarbon concentrate by nitration and reduction also raised the knock rating from 0.4 to 2.0; 3% of the mixed product from nitration and reduction of the 82% xylene concentrate above was similarly effective; and 3% of N methyl aniline raised the knock rating from 0.4 to 4.0. Similar effects may be obtained with

individual alkyl-substituted aromatic hydrocarbons of this invention, such as toluene, mixed xylenes, cumene, etc. Different amounts such as about 1% of these amines and about 5% of the aromatics, were also effective. All of the above blends of this paragraph had compatibility temperatures below about -50°F. , the blends containing meta xylene or cumene having compatibility temperatures below -76°F. and exhibiting unusually good anti-detonation properties.

The process of nitration and reduction used in converting aromatic hydrocarbon concentrates to amines may be exemplified by the following procedure which was used with the above 70% aromatic concentrate. A similar procedure was employed for the 82% xylene concentrate obtained from the hydroforming operation described earlier.

To a mixture of 2100 ml. of concentrated (96%) sulfuric acid and 1200 ml. of glacial acetic acid, cooled to about 20°F. , was added 3600 ml. (about 3000 g.) of the 70% aromatic concentrate. This mixture was cooled to about 0°F. and maintained between 0°F. and 10°F. while adding slowly with vigorous agitation a mixture of 1050 ml. of concentrated (70%) nitric acid and 2100 ml. concentrated (96%) sulfuric acid. This product mixture was then kept cold while diluting it with water sufficiently to prevent further reaction and to permit separation into two layers, a lower aqueous acid layer, and an upper layer which consisted of the crude nitro-aromatics containing unreacted oil and some products of side-reactions. Half of this upper layer was reduced by adding it to 1000 g. of water, and 200 g. of concentrated (37%) hydrochloric acid, and refluxing the mixture at 180°F. to 190°F. while slowly adding 2000 g. of iron. Agitation was continued for about 45 minutes, the mixture was cooled, the acid was neutralized with about 100 g. of caustic soda dissolved in water, and the mixture was distilled to recover about 1100 ml. of oil phase. The latter was redistilled with rough fractionation to obtain 400 ml. of a fraction distilling between 415°F. and 454°F. This fraction constituted the mixed amines used in the above example. The gravity of the mixture was about 14° API at 60°F. and it was practically completely soluble in 6 N hydrochloric acid. The remaining approximately 700 ml. of product was largely unreacted oil, but contained about 18% of unrecovered amines, and could also probably be used to advantage in aviation gasoline. The nitro-aromatics may also be reduced to amines by high pressure hydrogenation in a bomb, using an ammonium sulfide-iron sulfide catalyst.

Another phase of the present invention lies in the use of isopropyl ether in the aviation gasolines of this invention, together with the amines of this invention, and with or without the aromatic hydrocarbons of this invention. It has long been known that isopropyl ether is a very effective agent for improving the anti-knock value of aviation gasolines, yet its relative instability to oxida-

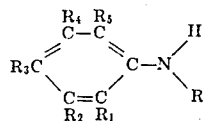
tion has militated against its widespread use, since upon oxidation it forms dangerously explosive peroxides. According to the present invention, 1% to 5% of the aromatic amines described are used in conjunction with 1% to 20% of isopropyl ether, thereby stabilizing the ether so as to prevent the formation of explosive peroxides with the consequent hazard and loss of knock rating. This ether also is effective in reducing the compatibility temperatures of amine-containing blends. The enhanced value of the amines in the presence of the aromatics may also be obtained in the presence of the isopropyl ether.

While I have described my invention employing tetraethyl lead as a knock-suppressing additive, I intend to include in the invention defined in the following claims not only tetraethyl lead and other alkyl lead compounds but also other knock-suppressing additives, such as nickel carbonyl, iron carbonyl, iron acetylacetonates, organic ferro- and ferri-cyanides, ferric compounds of oxymethylene camphor, heavy metal compounds of beta-diketones, etc.

There are modifications of the above described invention which will be obvious to those skilled in the art, and where these are not covered by earlier art, they are to be included in the scope of the following claims.

I claim:

1. An aviation-type gasoline having a compatibility temperature below about -50°F. , comprising a blend of about 0.5% to about 15% of an amine having 7 to 12 carbon atoms and having a structural formula as follows:



in which R_1 to R_6 inclusive are groups selected from the class consisting of hydrogen, phenyl, and saturated alkyl; more than about 5% of aromatic hydrocarbons having 7 to 10 carbon atoms; and a mixture of hydrocarbons boiling in the gasoline range other than said aromatic hydrocarbons having from 7 to 10 carbon atoms, with more than about 2 ml. per gallon of tetraethyl lead, said last named mixture of hydrocarbons with tetraethyl lead having an anti-knock rating at least equal to that of 2,2,4-trimethyl pentane.

2. A gasoline according to claim 1 in which the amine is a secondary amine.

3. A gasoline according to claim 1 in which the amine is N-methyl aniline.

4. A gasoline according to claim 1 in which the amine is a primary amine.

5. A gasoline according to claim 1 in which the amine is a xylidine.

6. A gasoline according to claim 1, containing also 1 to 20% of isopropyl ether and no substantial quantity of olefins.

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