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#### INHIBITOR AND MOTOR FUEL STABILIZED THEREWITH

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and motor fuels comprising hydrocarbons stabilized therewith, the inhibitors serving to inhibit or retard gum or resinous products forma-

tion, and in many cases serving also to retard discoloration and/or to retard reduction of antiknock properties.

Prior to the advent of the cracking process as a factor in the trade, the hydrocarbon motor

- 10 fuels generally employed were known as straightrun gasolines, and were produced either by simple distillation from crude petroleums or by absorption from casinghead gases. These soproduced hydrocarbon motor fuels were of an
- 15 essentially saturated character, containing only negligible amounts of unsaturated and cyclic hydrocarbons so that they underwent substantially no change when stored for long periods of time, particularly if reasonable protection from the
- 20 influence of air and light was provided. When motor fuels, known as cracked gasolines. became an important factor in the trade, it was found that their more unsaturated constituents,
- for example, di- and triolefins, were character-25 ized by a tendency to form gum or resinous products upon standing, particularly under the influence of air and light. This formation of gummy or resinous material was objectionable, in that gum in motor fuels is likely to deposit in
- 30 the induction system of the carburetor and intake valves, and even prevent the operation of the motor. The loss of certain of the unsaturated constituents during the gum formation was also objectionable, in that these constituents were
- 35 valuable as possible anti-knock material. During the gum-forming period a yellow or brown color sometimes developed.

The present invention is directed to the pre-

- vention of the formation of these undesirable 40 gums or resinous products and colored compounds and to the prevention of reduction in knock-rating in motor fuels comprising hydrocarbons and normally tending to deteriorate. However, it is to be particularly understood that
- 45 gum and color formation and reduction in knockrating are not necessarily related; the prevention or retardation of any one of these three undesirable tendencies may be accomplished independently, and, a motor fuel effectively stabilized 50 against gum formation may or may not undergo
  - discoloration or suffer a loss in knock-rating. In attempting to prevent or retard the formation of gum in motor fuels it has been proposed to add various organic compounds to the motor fuel.
- 55 Among these organic compounds, which, when dispersed in motor fuels, possess stabilizing properties are certain aminophenols, in which at least one hydrogen atom of the amino group is re-placed by an alkyl group, e. g., N-methyl-p-

60 aminophenol and N-benzyl-p-aminophenol, (N-

This invention relates to inhibitors (stabilize s) methyl and N-benzyl, in accordance with accepted chemical nomenclature, are intended to indicate that the methyl group or the benzyl group are attached to the nitrogen atom.) However, a number of these organic compounds, including the heretofore proposed nitrogen-alkylsubstituted aminophenols, while possessing the ability to stabilize motor fuels to a greater or lesser degree, suffer to a greater or lesser extent from one or more of the following disabilities 10 when used as stabilizers in connection with motor fuels consisting mainly of hydrocarbons: (1) low ultimate solubility therein, (2) slow rate of solubility therein, (3) lack of resistance to extraction by water and/or alkalies therefrom 15and (4) a tendency to impart or induce color and/or turbidity therein.

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Now, we have found that one or all of these above disabilities can be corrected, at least in part, by intimately mixing, advantageously prior 20 to dispersing in the motor fuel, the aminophenol, in which at least one hydrogen atom of the amino group is replaced by an alkyl group, with a phenylenediamine in which at least one hydrogen atom of each amino group is replaced by an alkyl 25 group. The phenylenediamine and the aminophenol apparently unite in some sort of loose chemical combination, and, the resulting combination, compared with the aminophenol, is characterized by increased ultimate solubility in the 30 motor fuel, increased rate of solubility in the motor fuel, increased resistance to extraction by water and alkalies from the motor fuel and decreased tendency to develop color and/or turbidity in the motor fuel. Phenylenediamines, in 35 which at least one hydrogen atom of each amino group is replaced by an alkyl group containing at least four carbon atoms, are particularly useful. In general maximum effects are obtained by employing a phenylenediamine, substituted as in- 40 dicated above, the total carbon atom, and the total hydrogen atom content of which are each equal to or greater than the total carbon atom and total hydrogen atom contents of the nitrogen-alkyl-substituted aminophenol. We have 35 further found that N-alkylamino-phenols and more particularly N-phimaryalkylaminophenols, in which the alkyl group contains at least four carbon atoms, intimately mixed with N,N'-dialkylphenylenediamines, particularly N,N'-di- 50 primaryalkylphenylenediamines, in which each alkyl group contains at least four carbon atoms, are very superior motor fuel stabilizers, some of them surpassing the best known motor fuel stabilizers in ability to inhibit gum formation, and, 55 nearly all of them surpassing the best known stabilizers in degree of solubility in motor fuels consisting mainly of hydrocarbons, in resistance to extraction by water and/or alkali therefrom and in showing little or no tendency to develop color 60 5

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and/or turbidity therein. (Primary alkyl group, in accordance with accepted chemical nomenclature, is intended to mean an alkyl group derived from a primary alcohol by dropping the OH group, e. g. from

CH3-CH-CH2CH2OH

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by dropping the OH group, one obtains

a primary alkyl group, viz. isoamyl.)

- Our new stabilizers are applicable to any motor fuel comprising hydrocarbons which normally, 15 i. e., without stabilization, undergoes deterioration, particularly deterioration characterized by gum or resinous products formation. Such motor fuels are commonly referred to under the names of gasoline, petrol, and the like, and contain, in 20 part or in whole, unstable constituents, such as
- unsaturated hydrocarbons of various sorts. These new stabilizers are particularly useful for stabilizing unsaturated hydrocarbon products or distillates, useful as motor fuels, produced by
- 25 cracking of higher boiling hydrocarbon oils, as well as for stabilizing blends of such products or distillates with the so-called straight-run distillates from petroleum. These new stabilizers are useful for stabilizing hydrocarbon products, use-
- 30 ful as motor fuels, produced by cracking or destructive distillation of substances rich in carbon and hydrogen, but containing a lesser proportion of hydrogen than hydrocarbon oils, such as bituminous materials, for example, coal, peat, lig-
- 35 nite and the like. These new stabilizers are also useful for stabilizing hydrocarbon products, useful as motor fuels, produced by the polymerization of unsaturated hydrocarbons, such as butenes, pentenes and the like.
- 40 The tendency of a motor fuel to form gum or resinous products can be determined, among other methods, by an accelerated oxidation test. While there are various methods of carrying out such a test, the method described by Egloff, Mor-
- 45 rell, Lowry and Dryer in Industrial and Engineering Chemistry, vol. 24, pages 1375-1378 (1932) is very satisfactory and is widely used. Briefly, the described method is as follows: A sample of the motor fuel, to be tested, in an
- 50 open eight-ounce bottle, is placed in a suitable metal bomb surrounded by a water bath. Oxygen is introduced to 100 pounds per square inch (7 kg. per sq. cm.) pressure. The bath is then heated by steam to 100° C. As the temperature
- 55 increases the pressure rises, reaches a maximum and continues near this maximum for a shorter or longer period of time. The test is continued for four hours or until a break in the pressure curve is noted. The period from slightly before
- 60 attainment of maximum pressure (approximately 15 minutes from the beginning of heating) until more than a slight drop in pressure takes place (usually a sharp break in the pressure curve occurs) is recorded as the induction period.
- 65 An induction period of less than 75 minutes is usually indicative of very low stability, while an induction period of 300 or more minutes for freshly made motor fuels or hydrocarbon products produced by cracking usually represents a
- 70 fuel possessing stability suitable for from about six to about twelve months bulk storage in the northern half of the United States. For more southern and warmer climates the induction period should be increased somewhat for satis-75 factory bulk storage of about a year's duration.

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mined on the freshly prepared motor fuel or hydrocarbon product produced by cracking since the induction period of partially aged material is probably not a reliable test.

In preparing our new motor fuel stabilizers, an intimate mixture of the desired aminophenol and the selected phenylenediamine can be prepared by melting the two substances together. A suitable method, which rids the mixture of any de- 10 composition products produced by melting, is to distil the mixture of aminophenol and phenylenediamine under sub-atmospheric pressure, pressures of 2 mm. or less being preferable. The intimate mixture can also be prepared by vigorous 15grinding or milling, or less satisfactorily by dissolving the ingredients in a common solvent, such as a suitable hydrocarbon, a mixture of hydrocarbons, an alcohol or a mixture of an alcohol and a hydrocarbon. Such solutions can be evap- 20 orated to dryness in order to obtain the solid intimate mixture, if desired. The proportion of aminophenol to phenylenediamine can advantageously be varied from about seventy-five to about ninety-five parts by weight of the amino- 25 phenol to from about twenty-five to about five parts of the phenylenediamine. We have found the ratios from about 80/20 to about 85/15 to be satisfactory in most cases. Larger proportions of phenylenediamine, for instance, a 50/50 ratio, 30 can be used, but are in most uses not necessary. Less than five parts of phenylenediamine have a beneficial effect. In general as the amount of phenylenediamine is increased from zero the intimate mixture becomes more and more soluble 35 in motor fuels, more and more resistant to extraction therefrom, etc. However the improvement is ordinarily at the expense of the motor fuel stabilizing potency of the intimate mixture and the ratios of aminophenol to phenylene- 40diamine indicated above are ordinarily suitable for practical purposes.

To prepare a stabilized motor fuel, the intimate mixture of aminophenol and phenylenediamine is added to the motor fuel in any of the generally  $_{45}$ accepted manners. Our stabilizers should be added to the freshly prepared motor fuel or hydrocarbon product, since partially aged materials usually cannot be effectively stabilized. While our new stabilizers are generally more soluble in 50motor fuels the ultimate solubility is not great and it is ordinarily advisable to observe the usual precautions regarding complete solution in the motor fuel. When stabilizing smaller quantities of motor fuel, up to 2000 barrel lots, our stabi- 55 lizers can be introduced directly into the tank or other container of freshly prepared motor fuel, by adding the stabilizer portionwise, using small portions, while vigorously agitating the stock being treated or causing the same to circulate, for 60instance, by pumping the contents of the lower part of the container to the top. Circulation or agitation of the stock being treated is advisable even after the addition of the stabilizer, in order to assure complete solution and no stratification. 65

In adding our new stabilizers to larger batches of motor fuels, the stabilizer can be added on the suction side of a pump in the form of a slurry in the motor fuel, or by means of a suitable feeding device, to a stream of the motor fuel, passing 70 to storage. The quantity of stabilizer added in such a manner should always be well below its maximum solubility in the motor fuel, and the pipe line to the storage tank should be long enough to allow the stabilizer to dissolve before 75

it reaches the storage tank. Undissolved stabilizer in the storage tank settles to the bottom and can only be dissolved with great difficulty. If not dissolved, the tank of motor fuel ordi-5 narily will not be uniformly stabilized.

Our new stabilizers can be added to a motor fuel by recirculating a stream of motor fuel through a small tank holding the stabilizer until a concentrated solution of the stabilizer is ob-10 tained. This concentrated solution can then be blended with the larger quantity of motor fuel to be stabilized. During this blending, precautions should be taken to avoid stratification.

Our new stabilizers can also be added to motor 15 fuels or hydrocarbon products in the form of solutions in solvents, such as alcohols, which are miscible or but partially miscible with the ordinary motor fuel. Any tendency of the stabilizer to precipitate and remain undissolved, when be-

- 20 ing added in this manner, can be offset by slower addition of the solution of stabilizer as well as by agitation and circulation of the stock being treated. Agitation and circulation are advisable, in any event, in order to avoid stratification.
- $_{25}$  Care should be exercised in selecting a solvent for the stabilizers, as certain solvents have a deleterious effect on the gum inhibiting ability of certain stabilizers. In general, alcohols are satisfactory media in which to dissolve our new sta-30 bilizers.

The quantity of our new stabilizers added to a motor fuel or hydrocarbon product will depend upon the quantity and kind of aminophenol in the composition, the type of motor fuel being 35 stabilized, and the conditions of storage. Usually an amount of one or more of our new stabilizers which give rise to a concentration of aminophenol equal to from about 0.01 g. to about 1.0 g. per 1000 g. of motor fuel or hydrocarbon products,

- 40 i. e., from about 0.001% to about 0.1% by weight. will suffice. In the case of an intimate mixture of N-primaryamyl-p-aminophenols (eighty-five parts by weight) and N,N'-diprimaryamyl-pphenylenediamines (fifteen parts by weight)
- from about 2.6 lbs. to about 7.9 lbs. per 1000 barrels of 42 gallons each (from about 0.001%) to about 0.003%) will be sufficient to provide an induction period of about 350 minutes, i. e., to provide stability for from 6 months to a year. Larger concentrations of the stabilizer can be
- 50 used, the length of the induction period being roughly proportional to the concentration, at least in the region of lower concentrations. Ordinarily, however, each motor fuel to be stabilized
- 55 required a separate test, the details of making which are described above. Modifications of the hereinabove described test and other tests are well known to those skilled in the art of manufacturing stabilized motor fuels.
- Among others, the aminophenols and phenyl-60 enediamines which can be used in practicing our invention are:

### **A**minophenols

N-methyl-p-aminophenol 65 N-ethyl-p-aminophenol N-n-propyl-p-phenylenediamine N-n-butyl-p-aminophenol N-n-amyl-p-aminophenol N-benzyl-p-aminophenol J N-methyl-o-aminophenol N-benzyl-N-methyl-p-aminophenol

- N-cyclohexyl-p-aminophenol
- N-methyl-m-aminophenol
- 2-methylamino-4-nitrophenol
- 75 2-methylamino-5-methyl-phenol

#### **Phenylenediamines**

N.N'-dimethyl-p-phenylenediamine N,N'-diethyl-p-phenylenediamines N,N'-dipropyl-p-phenylenediamines N,N'-dibutyl-p-phenylenediamines N,N'-diamyl-p-phenylenediamines N,N'-dibenzyl-p-phenylenediamine N,N'-dimethyl-o-phenylenediamine N,N'-dimethyl-m-phenylenediamine N,N,N',N'-tetramethyl-p-phenylenediamine

Neither the amine group of the aminophenol nor the amine groups of the phenylenediamine should be (NH<sub>2</sub>), nor should the amine groups of the phenylenediamine be arylamino groups, though phenylenediamines in which the amine groups are substituted alkylamino such as benzylamino groups are satisfactory.

The following table illustrates the increase in resistance to water and alkali extraction which one of our new stabilizers possesses over ordinary N-alkylaminophenols. In the case illustrated below, the stabilizer was dissolved in a standard reference motor fuel and the stabilized motor fuel was shaken for 10 minutes with 10% (by 23 volume) of distilled water, the water separated and the induction period determined. In the case of alkali, the stabilized motor fuel was shaken for 10 minutes with 5% (by volume) of a 1%solution of sodium hydroxide in water. 39

Table	Ι
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	N-methyl-p- aminophenol	N-methyl-p- aminophenol ad- mixed with 20% by weight of N,N'- dimethylphenyl- enediamine	35
A. Water extraction	Minutes	Minutes	
Induction period of stabi-	Intenanco	Intenanco	40
lized motor fuel after			
shaking with water Induction period of stand-	315	330	
ard reference motor fuel	220	220	
Increase in induction per- iod owing to stabilizer	95	110	
B. Caustic extraction			45
Induction period of stabi- lized motor fuel after shaking with caustic so-			• .
lution	215	225	
Induction period of stand- ard reference motor fuel	185	185	•
Increase in induction per-			50
iod owing to stabilizer	30	40	

From these data under A, it can be seen that water removes N-methyl-p-aminophenol from motor fuels more readily than a mixture of N- 55methyl-p-aminophenol and N,N'-dimethyl-pphenylenediamine, the latter giving an induction period 15.8% greater than the former following the water treatment. In the case of caustic treatment under B, the mixture gives an CO induction period 33.3% greater than that produced by N-methyl-p-aminophenyl. A mixture of N-amyl-p-aminophenols with about 15% by weight of N,N'-diamyl-p-phenylenediamines shows a similar improvement over N-amyl-p- 65 aminophenols alone.

We have also found that excellent motor fuel stabilizers, which analyses indicate are compositions of matter containing aminophenols and reaction products of higher molecular weight than 70 the aminophenols, e.g. phenylenediamines, can be prepared directly from a polyhydric phenol containing at least two phenolic hydroxyl groups in the ortho or para position to one another and a higher primary or secondary alkyl primary 75

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amine, i. e. one having at least four carbon atoms. This is accomplished by reacting the phenol and the amine under such conditions that water is eliminated between the phenol and amine. Reaction is advantageously effected in the substantial absence of diluents other than the diluents,

e. g. water, formed during the reaction. The amine is advantageously employed in molecular excess. The reaction products, analyses indicate, com-

1.1 prise principally N-alkylaminophenols and a number of attendant reaction products. Ordinarily one of these attendant reaction products is apparently a N,N'-dialkylphenylenediamine.

- 1.5 Whether our new reaction products are strictly mixtures or whether the ingredients are combined in chemical combination is not known. However, the reaction products do not behave as mixtures in that it has proven impossible to sep-2) arate the various ingredients by fractional dis-
- tillation, or, to separate the aminophenols from the reaction products by ordinary chemical means. The motor fuel stabilizing properties of these new reaction products resides partly, and 2. perhaps mainly in the N-alkylaminophenols and
- partly in the attendant reaction products. The N,N'-dialkylphenylenediamines ordinarily possess lesser powers of stabilizing motor fuels, but tend to make the new compositions of matter
- 30 more readily soluble in motor fuels comprising substantial proportions of hydrocarbons, more resistant to extraction by water therefrom and less likely to develop color and/or turbidity there-The attendant reaction products other than in.
- 3. phenylenediamines likewise confer these latterstated properties upon these new compositions of matter, in addition to contributing to the motor fuel stabilizing properties. The better reaction products for the stabilization of motor
- 40 fuels appear to contain a weight of attendant reaction products equal to from about 5 to about 25 percent of the total weight of both the principal and attendant reaction products. Smaller amounts of the attendant reaction products have  $_{45}$  a beneficial effect and reaction products contain-
- ing 50 percent by weight of attendant reaction products can be used as motor fuel stabilizers. The polyhydric phenols employed can be sub-

stituted on the nucleus by groups such as methyl,  $_{50}$  methoxyl and the like. Catechol, hydroquinone and pyrogallol yield powerful motor fuel stabi-

- lizers, but from all standpoints those stabilizers, prepared as indicated above, from either unsubstituted catechol or hydroquinone, especially the 5.5 latter, are particularly advantageous for the
- usual stabilization, and, our new stabilizers will be described with particular reference to the reaction products of the dihydric phenols, in particular hydroquinone.
- Primary amines, such as normal primary 60 butyl, normal secondary butyl, isobutyl, normal primary amyl, isoamyl, isohexyl and neopentyl, as well as mixtures thereof can be used. The higher primary amine is advantageously employed
- 65 in molecular excess, from about one and onequarter to about two and one half molecular proportions for each molecular proportion of polyhydric phenol being particularly useful. Proportions outside these advantageous limits can
- 70 be used. However, as the moles of amine per mole of phenol are increased above two and onehalf, the resulting compositions of matter will be found to become less and less potent as motor fuel stabilizers, while less than one and one-75 quarter moles of amine yield compositions of

matter gradually decreasing in effectiveness as motor fuel stabilizers and also gradually decreasing in solubility in motor fuels, in resistance to extraction therefrom, etc. With pyrogallol about 2.5 moles of amine are advantageously 5 employed.

Ordinarily no diluent other than the impurities found in the usual commercial amine (about 10% by weight or less of water, alcohol, etc.) should be used. As the reaction mixture is diluted from 10 these advantageous concentrations, the reaction products will be found to become less and less soluble in motor fuels, less and less resistant to extraction therefrom, etc.

In preparing our new reaction products a mix- 15 ture of polyhydric phenol, the polyhydric phenol advantageously being in solution in the excess amine, is heated, advantageously, in a closed system such as an autoclave, at about 200° C. until the reaction becomes slow and practically 20 ceases, e.g., for about 20 hours. The condensation can be effected at temperatures as low as 150° C., and as high as 250° C. without great difficulties. However, at the lower temperatures longer reaction times (20 to 30 hours) are neces- 25 sary, while at the higher temperatures shorter reaction times (12 to 20 hours) suffice. Temperatures much higher than 250° C. are in general unsatisfactory and for that reason precautions to avoid local heating should be taken. This can 30 be done by agitating the reaction mass. Prolonged heating at any temperature should be avoided, since even at 200° C, or less, undesirable changes will slowly take place if heating is continued much beyond the optimum times stated, 35 e. g. at 200° C. for 20 hours. In a closed system, the pressure rises to about 225 pounds per square inch at 200° C. when amylamines are used and to somewhat higher pressures when butylamines are used. During the reaction, water is formed. 40 This water of formation and any unreacted amine is distilled off following completion of the reaction. The amine thus recovered is separated from the water which also distills by any suitable means. 45

Thus, it is apparent that we carry our reaction to substantial completion with respect to the polyhydric phenol. We ordinarily stop the reaction slightly short of the point where the polyhydric phenol is completely reacted rather than allow 50 the reaction to proceed until the last trace of polyhydric phenol is reacted, thereby avoiding the formation of undesirable (usually tarry) products as much as possible.

We can subject our new reaction products to 55 distillation under reduced pressure in order to effect a purification. Pressure of 2 mm. of mercury or less are preferable. So distilled, our products are pale yellow liquids which solidify slowly on standing. The distillation rids the prod- $_{60}$ ucts of suspended carbonaceous and tarry matter but does not serve to separate the products into discreet substances.

The secondary alkyl primary amines appear to react at a slower rate than the primary alkyl  $_{65}$ and therefore the higher of the above reaction temperatures are advantageously employed when using the secondary alkyl derivatives. The commercial primary amines available frequently are made up of mixtures of primary and secondary 70 alkyl primary amines and because of the slower reaction of the secondary they will ordinarily be found to accumulate in the recovered amine. The reaction products made from the secondary alkyl primary amines while good motor fuel stabilizers 75

are not as desirable as those made from the primary alkyl primary amines. We have found that the reaction products from the secondary alkyl derivatives are most advantageously used in conjunction with the reaction products of the primary alkyl derivatives by admixing a small amount of former with a relatively large amount of the latter.

Reaction products (prepared as indicated above) of polyhydric phenols and methyl, ethyl 10 or propyl amines are largely N-alkylaminophenols sometimes together with N,N'-dialkylphenylenediamines. However, such reaction products differ from those described above in that those pre-

- 15 pared from amines of three carbon atoms or less are much less soluble in motor fuels consisting mainly of hydrocarbons and in that the aminophenols can be separated therefrom by ordinary chemical means, the propyl derivative offering the greatest difficulty and resembling the reaction
- 20 product made from the butyl or higher amines to some extent in this respect.

The following example serves to illustrate the preparation of one of our new condensation 25 products. However, we do not intend that this example limit our invention.

557 lbs. (about 6.0 mols) of commercial primaryamylprimaryamine (usually containing from about 5% to about 10% by weight of water and other inert materials, usually having a boil-30 ing range from about 85° C. to about 105° C. and comprising a plurality of isomeric amines) were charged into a still provided with an agitator, a simple fractionating column, steam and cooling coils, surface condenser and an automatic liquid 35

separator. 300 lbs. (2.7 mols) of hydroquinone were added and the whole was agitated until

solution of the hydroquinone was effected. Heat may be applied to effect this solution. This so prepared solution was conveyed to an autoclave and heated therein at about 200° C. for about 20 hours. Following this treatment the reaction mixture was subjected to distillation in a rapid circulating evaporator, when the excess amylamine and the water of formation distilled off. The residue was thoroughly dried and degassed of remaining traces of amylamine. The degassed material was transferred to a high vacuum still and distilled under a pressure of about 2 mm. or less. The product is a pale yellow liquid which solidifies slowly on standing. The product needs no further purification. It can be used as a motor fuel stabilizer in the solid form, but is preferably introduced into the motor fuel from 50% (weight) solution in a solvent composed of 90% methanol and 10% butanol or other suitable solvent.

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The excess amylamines and the water of for-20 mation which distilled off from the rapid circulating evaporator were returned to the mixing tank and the amylamines recovered.

In preparing our new reaction products, as indicated above, catalysts can be added to the re-25 action mixture or the amines can be employed in the form of derivatives which decompose under the conditions of the reaction to yield the amine.

The following table shows the excellent properties as a motor fuel stabilizer which one of our 30 new reaction products of a higher primaryalkylprimaryamine and a dihydric phenol possesses as compared with the properties of some of the best known motor fuel stabilizers. The reaction product of hydroquinone and a mixture of primaryamylprimaryamines dealt with in this table was prepared according to the above example.

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40		Condensation product of hydroquinone and a mixture of amylamines	N-benzyl-p-amino- phenol	N-methyl-p-amino- phenol	Wood tar distillate	40
	1. Stabilizing potency (accelerated oxidation)					
45	a. Percent conc. of stabilizer in motor fuel b. Percent conc. of aminophenols in motor fuel c. Moles of aminophenols per 1,000 gm. of motor	0.00125 0.00100* 0.000058	0.00125 0.00125 0.000063	0.00125		45
	fuel. d. Induction period of standard reference motor fuel (min.).	150.0				
60	<ul> <li>e. Induction period of stabilized motor fuel (min.)</li> <li><i>i</i>. Increase in induction period owing to stabilizer (min.).</li> </ul>	395.0 245.0	290.0 140.0	410.0 260.0	170. 4 20. 4	50
	2. Solubility in motor fuel					
	Percent of stabilizer by weight 25° C	1.5**	0.2**	0.008***		
	3. Resistance to water extraction			and a second second Second second		55
55	Stabilized motor fuel shaken 3 times with water. Expressed as percent decrease in effectiveness.	1.0	28.5	74.0	37.0	
	4. Resistance to alkali extraction		No. In the second s			
60	Stabilized motor fuel shaken once with 1% aqueous sodium hydroxide. Expressed as percent decrease in effectiveness.	54.8	91.0	91		60
	5. Color stability of stabilized motor fuel					
	Concentration of stabilizer in motor fuel (percent	0.01	0.01	0.0005		
65	by weight). Stabilized motor fuel in glass container exposed to diffused light.	No color or haze after 48 hours. No color in motor fuel	Slight precipitate after 48 hours. Water layer brown	No color or haze after 48 hours. Water layer brown		05
• • •	Stabilized motor fuel over iron and water Stabilized motor fuel in glass container exposed to direct sunlight01% stabilizer by weight, ex- cept N-methyl-p-aminophenol which was tested at .005% by weight.	or water after 6 days. No haze or color after 3 hours.	after 3 hours. Slight haze and yellow color after 3 hours.	after 3 hours. Slight haze and yellow color after 1 hour.		•
-70	6. Solubility in methanol					70
	Percent of stabilizer by weight (25° C.)	62.0	About 50	Less than 50		

Estimated from analytical data.
 Determined by adding 50% solution of stabilizer in methanol to the motor fuel.
 Determined by adding 40% solution of stabilizer in methanol to the motor fuel.

From the data given in the above table, it is clear that our new reaction products, prepared by a process comprising reacting a dihydric phenol and a higher primaryalkylprimaryamine, in the 5 substantial absence of diluents, the reaction prod-

uct containing a substantial proportion of an attendant reaction product of higher molecular weight than the principal reaction product, viz. a N-alkylaminophenol, are far superior to the best 10 known stabilizers in ability to prevent or retard

- gum formation in motor fuels or hydrocarbon products. The markedly greater solubility of this group of our new stabilizers in motor fuels assures an adequate concentration of stabilizer even
- 15 after a considerable amount has been dissipated in the prevention of gum. This inherent greater solubility also allows our new stabilizers to be dispersed more readily in the ordinary hydrocarbon motor fuels. This group of our new stabi-
- 20 lizers are exceptional in their remarkable resistance to extraction from motor fuels by water; they also neither impart nor induce color and/or turbidity to the motor fuel under ordinary conditions. These new stabilizers show increased solu-
- 25 bility in alcohols, an important factor when adding the stabilizers to motor fuels from alcoholic solutions. This group of our new stabilizers have no deleterious effect on the dyes ordinarily employed to color motor fuels. These reaction prod-
- 30 ucts are further described in our copending application Serial No. 96,466, filed August 17, 1936. Other motor fuel stabilizers can be used in conjunction with our new stabilizers if desired. Substances used primarily to stabilize color, such as
- as di and tributylamine and triamylamine can be used in conjunction with our new stabilizers. Anti-knock agents can be used in conjunction with our new stabilizers.

What we claim as our invention and desire to 40 be secured by Letters Patent of the United States of America is:

1. A liquid motor fuel comprising light hydrocarbons and normally tending to deteriorate containing, in an amount sufficient to substantially

- 45 retard such deterioration, an aminophenol capable of inhibiting the formation of gum or resinous products in said motor fuel and having at least one hydrogen atom of the amino group replaced by an alkyl group containing at least four carbon
- 50 atoms, together with a substantial proportion. based upon the amount of the aminophenol, of a phenylene diamine having at least one hydrogen atom of each amino group replaced by an alkyl group containing at least four carbon atoms.
- 2. A liquid motor fuel comprising light hydro-**#**5 carbons and normally tending to deteriorate containing, in an amount sufficient to substantially retard such deterioration, a N-alkyl-p-aminophenol capable of inhibiting the formation of gum
- •0 or resinous products in said motor fuel and in which aminophenol the alkyl group contains at least four carbon atoms, together with a substantial proportion, based upon the amount of the aminophenol, of a N,N'-dialkyl-p-phenylenedi-
- es amine in which each alkyl group contains at least four carbon atoms.

3. A liquid motor fuel comprising light hydrocarbons and normally tending to deteriorate containing, in an amount sufficient to substantially

70 retard such deterioration, a N-primary alkyl-paminophenol capable of inhibiting the formation of gum or resinous products in said motor fuel and in which aminophenol the primary alkyl group contains at least four carbon atoms, to-75 gether with a substantial proportion, based upon the amount of the aminophenol, of a N,N'-diprimary alkyl-p-phenylene diamine in which each primary alkyl group contains at least four carbon atoms.

4. A liquid motor fuel comprising light hydro- 5 carbons and normally tending to deteriorate containing, in an amount sufficient to substantially retard such deterioration, a N-primary-butyl-paminophenol capable of inhibiting the formation of gum or resinous products in said motor fuel, 10 together with a substantial proportion, based upon the amount of the aminophenol, of a N,N'diprimarybutyl-p-phenylenediamine.

5. A liquid motor fuel comprising light hydrocarbons and normally tending to deteriorate con- 15 taining, in an amount sufficient to substantially retard such deterioration, a N-primary-amyl-paminophenol capable of inhibiting the formation of gum or resinous products in said motor fuel, together with a substantial proportion, based 20 upon the amount of the aminophenol, of a N,N'diprimaryamyl-p-phenylenediamine.

6. A liquid motor fuel comprising light hydrocarbons and normally tending to deterioration containing, in an amount sufficient to substan- 25 tially retard such deterioration, a reaction product comprising a substantial quantity of an aminophenol having at least one hydrogen atom of the amino group replaced by an alkyl group containing at least four carbon atoms, together 80 with a substantial proportion, based upon the quantity of the aminophenol, of a phenylenediamine having at least one hydrogen atom of each amino group replaced by an alkyl group contain ing at least four carbon atoms, said reaction 35 product being produced by the substantially complete reaction of hydroquinone with at least an equimolecular proportion of an alkyl primary amine containing at least four carbon atoms, at a temperature of from about 150° C. to about 40 250° C.

7. A liquid motor fuel comprising light hydrocarbons and normally tending to deterioration containing, in an amount sufficient to substantially retard such deterioration, a reaction prod- 45 uct comprising a substantial quantity of an aminophenol having at least one hydrogen atom of the amino group replaced by a primary butyl group, together with a substantial proportion, based upon the quantity of the aminophenol, of 50 a phenylenediamine having at least one hydrogen atom of each amino group replaced by a primary butyl group, said reaction product being produced by the substantially complete reaction of hydroquinone with at least an equimolecular pro- 55 portion of a primary butyl primary amine containing at least four carbon atoms, at a temperature of from about 150° C. to about 250° C.

8. A liquid motor fuel comprising light hydrocarbons and normally tending to deterioration 60 containing, in an amount sufficient to substantially retard such deterioration, a reaction product comprising a substantial quantity of an aminophenol having at least one hydrogen atom of the amino group replaced by a primary amyl 65 group, together with a substantial proportion, based upon the quantity of the aminophenol, of a phenylenediamine having at least one hydrogen atom of each amino group replaced by a primary amyl group, said reaction product being pro- 70 duced by the substantially complete reaction of hydroquinone with at least an equimolecular proportion of a primary amyl primary amine containing at least four carbon atoms, at a temperature of from about 150° C. to about 250° C. 75

9. A process for preparing a stabilized liquid motor fuel comprising light hydrocarbons and normally tending to deteriorate comprising dissolving in the motor fuel, in an amount sufficient to substantially retard such deterioration, an aminophenol capable of inhibiting the formation of gum or resinous products in said motor fuel and having at least one hydrogen atom of the

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amino group replaced by an alkyl group contain-10 ing at least four carbon atoms, together with a substantial proportion, based upon the amount of the aminophenol, of a phenylene-diamine having at least one hydrogen atom of each amino group replaced by an alkyl group containing at least 15 four carbon atoms.

10. As a stabilizer for a liquid motor fuel com-

prising light hydrocarbons and which normally tends to deteriorate, a composition of matter comprising a substantial amount of an aminophenol capable of inhibiting the formation of gum or resinous products in said motor fuel and having 5 at least one hydrogen atom of the amino group replaced by an alkyl group containing at least four carbon atoms, together with a substantial proportion, based upon the amount of the aminophenol, of a phenylenediamine having at least one 10 hydrogen atom of each amino group replaced by an alkyl group containing at least four carbon atoms.

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