Oct. 13, 1959 M. R. BRIMER 2,908,558

GUM INHIBITORS FOR GASOLINE

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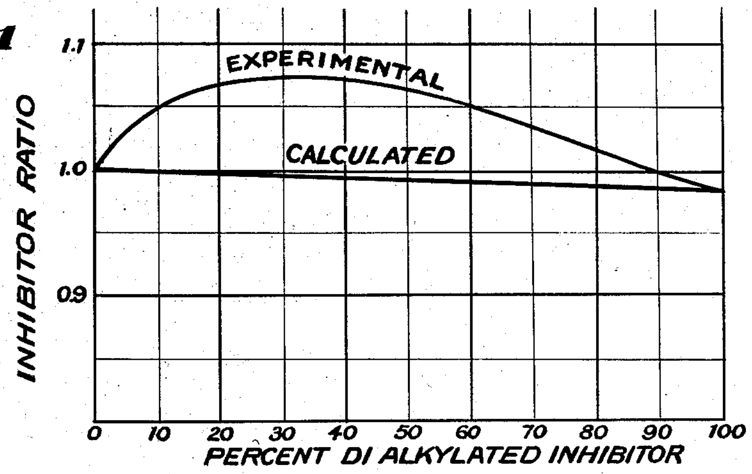
Fig.1



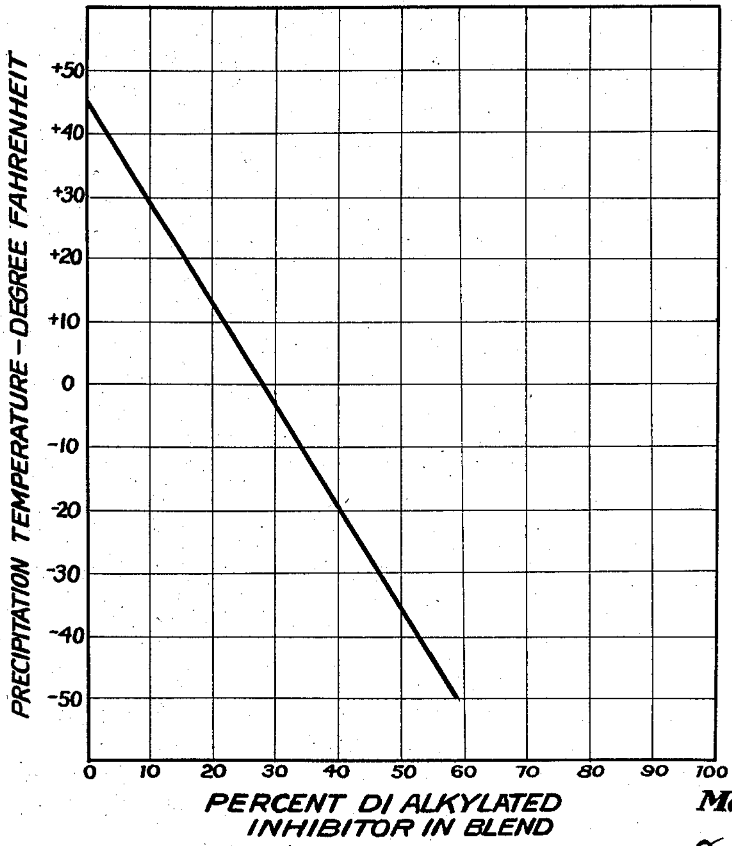


Fig.2

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GUM INHIBITORS FOR GASOLINE

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This invention relates to synergistic gum inhibitors for gasoline and to stabilized gasoline compositions.

Motor fuels and particularly gasolines containing a substantial amount of thermally or catalytically cracked stocks are normally subject to gum formation. The N-monoalkyl-p-aminophenols are used widely for effectively obviating objectionable gum formation, usually admixed with about 10% by weight of N,N′-dialkyl-p-phenylene diamine, and such inhibitors are commonly added to the gasoline as a solution in a suitable organic solvent such as an alcohol or the like.

It is an object of this invention to provide improved gum inhibitors comprising a mixture of components exhibiting synergistic inhibitor activity.

It is a further object of this invention to stabilize gasoline with a new and improved synergistic inhibitor composition, and particularly with a synergistic inhibitor composition, having unusual solubility properties and a much lower precipitation temperature than would be expected from the individual components thereof.

Another object of the invention is to provide mixtures of an N-monoalkyl-p-aminophenol and an N,N-dialkyl-p-aminophenol which exhibit gum inhibiting potencies higher than would be expected from the potencies of the individual components of the mixture, and particularly to provide such mixtures containing a substantial amount of an N,N′-dialkyl-p-phenylene diamine.

Another object of the invention is to provide improved gum inhibitor compositions whereby the inhibitor can be used in lower amounts than was possible with the N-monoalkyl-p-aminophenols alone to give a desired inhibiting action, or conversely whereby an equal level of the improved inhibitor of this invention will give a higher level of inhibiting action than will the prevously employed N-monoalkyl-p-aminophenol.

Other objects of the invention will be apparent from the description and claims which follow.

These and other objects are attained by means of this invention as described more fully hereinafter and illustrated in the drawings and as defined in the appended claims. I have found that mixtures of an N-monoalkyl-p-aminophenol and an N,N′-dialkyl-p-aminophenol exhibit a synergistic inhibiting effect on gum formation in motor fuels which is substantially higher than to be expected from the inhibiting action of the components considered individually. This synergistic effect is apparent with the various combinations of N-monoalkyl-p-aminophenols and N,N-dialkyl aminophenols wherein the various alkyl groups contain 1–6 carbon atoms. The alkyl groups can be the same or different alkyl groups as defined; and, as described hereinafter, particularly good results are obtained when the alkyl groups in the dialkylated material differ either in number of carbon atoms or structural configuration or both. Particularly advantageous results are obtained with mixtures of N-n-butyl-p-aminophenol and N-n-butyl-N-isobutyl-p-aminophenol. From the standpoint of solubility and precipitation temperature, the synergistic mixtures desirably contain a substantial amount, i.e. 5–20%, and preferably about 10% by weight of N,N′-dialkyl-p-phenylene diamine based on the weight of the N-monoalkyl-p-aminophenol.

The improved results obtained with the preferred compositions embodying the invention are illustrated in the drawings.

Fig. 1 illustrates the synergistic effect in gasoline observed with mixtures of N-n-butyl-p-aminophenol and N-n-butyl-N-isobutyl-p-aminophenol, containing 10% of N,N′-di-n-butyl-p-phenylene diamine based on the weight of the N-n-butyl-p-aminophenol, as contrasted with the calculated activity to be expected from the activity of the individual components over the entire range from 0% to 100% of each of the monoalkyl and the dialkyl aminophenols. The inhibitor ratio is the ratio of the inhibitor activity of the new mixture to the inhibitor activity, taken as 1.0, of a mixture of 90% by weight of N-n-butyl-p-aminophenol and 10% by weight of N,N′-di-n-butyl-p-phenylene diamine.

Fig. 2 illustrates the improved precipitation temperature obtained with the mixtures of Fig. 1 at a 20% level in straight run gasoline, the composition at 0% dialkylated inhibitor consisting of a mixture of 90% by weight of N-n-butyl-p-aminophenol and 10% by weight of N,N′-di-n-butyl p-aminophenol.

As can be seen from Fig. 1, the synergism is apparent over the entire range of concentrations. Because of the lower individual potency of the dialkylated inhibitor, however, the activity of the blend is lower than that of the monoalkylated inhibitor in the range of 90–100% of the dialkylated inhibitor even with the synergistic action. Consequently, the preferred compositions comprise a mixture of 1–90% by weight of N-n-butyl-N-isobutyl-p-aminophenol and 99–10% by weight of N-n-butyl-p-aminophenol, with the optimum activity in the range about 20–50% of dialkylated inhibitor and 80–50% of monoalkylated inhibitor. The compositions desirably employed are those in the range of 25–35% by weight of N-n-butyl-N-isobutyl-p-aminophenol and 75–65% by weight of N-n-butyl-p-aminophenol with or without about 10% by weight of N,N′-di-n-butyl-p-phenylene diamine based on the weight of N-n-butyl-p-aminophenol.

Similar mixtures of N-n-butyl-p-aminophenol and N,N-di-n-butyl-p-aminophenol also show synergism over the entire range of proportions, but the inhibitor ratio drops below 1.0 at about 65% concentration of the dialkyl component, and hence this blend is less desirable. Furthermore, the preparation of the N-n-butyl-N-isobutyl-p-aminophenol is preferred because of economic reasons, and, in the preferred catalytic process, catalyst poisoning is reduced.

The N,N-dialkyl-p-aminophenols can be prepared by any desired method. In one process, p-nitrophenol can be reacted with an alkyl aldehyde in the presence of hydrogen and a hydrogenation catalyst, in an organic solvent which is preferably the alcohol corresponding to the aldehyde employed. In this case, the alkyl groups in the mixture of monoalkylated inhibitor and dialkylated inhibitor obtained are the same. This method of preparation is illustrated by the following examples.

EXAMPLE 1

A mixture of 70.0 g. (0.5 mole) of p-nitrophenol, 10.0 g. of Raney nickel and 159.3 g. (2.16 moles) of n-butanol was charged to an autoclave and 620 p.s.i. of hydrogen was applied. The autoclave was warmed to 60–65° C., and a mixture of 190.0 g. (2.64 moles) of n-butyraldehyde and 12.9 g. (0.175 mole) of n-butanol was fed in under pressure over a 3.5 hour period. The reaction was continued for an additional 3.75 hours, and thereafter the autoclave was cooled and vented, and the reaction mixture was removed and filtered to remove the catalyst. The low boiling components were removed under reduced pressure, leaving 100.3 g. of crude product. This crude product when distilled at further reduced pressure yielded 91.1 g. of product and 6.3 g. of residue. The product contained 23.6% of essentially N,N-di-n-butyl-p-aminophenol and 74.4% which was essentially N-n-butyl-p-aminophenol. This product was separated into a caustic soluble fraction and a caustic insoluble fraction and the inhibitor activity in Pennsylvania cracked gasoline at a 0.0048 weight percent concentration of inhibitor was determined by the Active Oxygen Method and compared with a standard inhibitor consisting of 90% by weight of N-n-butyl-p-aminophenol and 10% by weight of N,N′-di-n-butyl-p-phenylene diamine. The inhibitor ratio was also calculated based on the inhibitor ratio of the standard taken as 1.0.

Table 1

Additive	Induction Period—Minutes			
	Blank	Test	Standard	Inhibitor Ratio
Caustic Insoluble Component	40	275	490	0.52
Caustic Soluble Component	40	532	490	1.11
Blend:				
23.6% Caustic Insoluble	40	517	490	1.07
76.4% Caustic Soluble				

From the inhibitor activities of the two fractions, the calculated inhibitor ratio of the blend is only 0.97 whereas the actual inhibitor ratio found experimentally was 1.07. This clearly demonstrates the synergistic effect of the blend.

The effective inhibitor action of the blends as compared to N-n-butyl-p-aminophenol when used at a 0.01% concentration in a Pennsylvania blend of catalytic and thermally cracked gasoline is shown in Table 2.

Table 2

Additive	Effective Inhibitor Ratio	Calculated Inhibitor Ratio
N-n-butyl-p-aminophenol	1.00	----------
N,N-di-n-butyl-p-aminophenol	0.92	----------
3 parts N-n-butyl-p-aminophenol	1.055	0.98
1 part N,N-di-n-butyl-p-aminophenol		
35 parts N-n-butyl-p-aminophenol	0.99	0.95
65 parts N,N-di-n-butyl-p-aminophenol		

In the preferred process, N-monoalkyl-p-aminophenol, with or without N,N′-dialkyl-p-phenylene diamine, is reacted with an alkyl aldehyde in the presence of hydrogen and a hydrogenation catalyst in an organic solvent. By this means, the alkyl groups in the dialkylated inhibitor can be the same or different depending upon the alkyl aldehyde employed. This process can be carried only partially to completion whereby a mixture of monoalkyl and dialkyl inhibitor results, but it is often difficult to control the amount of alkylation to give the desired mixture. Consequently, it is preferred to convert the N-monoalkyl-p-aminophenol completely to the dialkylated inhibitor and then blend this product with monoalkylated inhibitor to the desired composition.

In this process as in the process illustrated in Example 1, Raney nickel is the preferred catalyst although other hydrogenation catalysts can be successfully employed such as supported nickel catalysts, platinum or palladium catalysts, copper chromite catalysts and the like. The choice of operating conditions depends largely on the catalyst employed. If the catalyst employed is the preferred Raney nickel, the process can be operated successfully over a temperature range of 25° C. to 120° C. and a hydrogen pressure range of 500 to 5000 p.s.i. The time required for the process will vary with the temperature and pressure; since an increase in either variable will decrease the time required. In the process wherein monoalkyl-p-aminophenol is converted, the preferred conditions are a temperature of 40° C. to 100° C. with hydrogen pressure of 1000 p.s.i. to 2500 p.s.i. using a Raney nickel catalyst. Under these conditions, the process requires about 30 minutes to 2 hours for completion when carried out batchwise in a standard rocking autoclave. If a supported nickel catalyst is used, a longer time is required and the operating temperature range is 100° C. to 150° C. A copper chromite catalyst requires an operating temperature range of 125° C. to 175° C. With platinum or palladium catalysts, the optimum temperature range is 25–50° C. and a hydrogen pressure of 15–150 p.s.i. will suffice.

The process can be carried out in the absence of a solvent or in the presence of a solvent. Usually it is desirable to use a solvent which corresponds to the byproduct of the reaction, i.e. methanol with formaldehyde, ethyl alcohol with acetaldehyde, n-butanol with n-butyraldehyde, isobutyl alcohol with isobutyraldehyde, and the like. The advantageous characteristics of the preferred mixture of N-n-butyl-p-aminophenol and N-n-butyl-N-isobutyl-p-aminophenol are illustrated in the following example.

EXAMPLE 2

A mixture of 9 parts of N-n-butyl-p-aminophenol and one part of N,N′-di-n-butyl-p-phenylene diamine was alkylated with isobutyraldehyde in isobutanol and in the presence of hydrogen and Raney nickel. The reaction mixture was filtered to remove the catalyst. The low boiling components were removed by distillation and the remaining crude base material was distilled at 2 mm. pressure. The effective inhibitor ratio of the resulting dialkylated product as well as blends of the product with the original inhibitor mixture were determined by the Active Oxygen Method at a 0.01% concentration of additive in a Pennsylvania blend of thermal and catalytic cracked gasoline. The "base" in Table 3 designates a mixture of 9 parts of N-n-butyl-p-aminophenol and 1 part of N,N′-di-n-butyl-p-phenylene diamine.

Table 3

Additive	Effective Inhibitor Ratio	Calculated Inhibitor Ratio
Base	1.00	----------
Distilled dialkylated product	0.985	----------
1 part Distilled product	1.055	0.99
3 parts Base		
35 parts Distilled product	1.065	0.985
65 parts Base		
1 part Distilled product	1.068	0.982
1 part Base		

The preferred blends as illustrated in Example 2 not only exhibit synergistic inhibitor activity over the entire concentration range as shown in Fig. 1, but they also have the advantage of precipitating from gasoline only at much lower temperatures than does the base mixture as shown in Fig. 2. Thus, as shown in Fig. 2, when a 52% solution of inhibitor in isopropanol was added to straight run gasoline to give a 20% concentration of inhibitor, the precipitation temperature decreases rapidly from +45° F. for the base mixture of 9 parts of N-n-butyl-p-aminophenol and 1 part of N,N′-di-n-butyl-p-phenylene diamine down to —50° F. when the blend consists of 40% of the base and 60% of N-n-butyl-N-isobutyl-p-aminophenol.

The synergism is also apparent with other blends of monoalkylated and dialkylated aminophenols. Of the blends, those wherein the dialkylated inhibitor contains two alkyl groups which differ either in number of carbon atoms or in structural configuration are preferred. In those cases, where one of the alkyl groups contains less than four carbon atoms, the dialkylated inhibitor is often as active or more active than the base inhibitor and hence there is less advantage in employing such materials in blends despite the synergism evidenced by such blends. Such blends are within the scope of the invention, however, and often may be desirable to use because of factors other than the inhibiting action alone.

EXAMPLE 3

A mixture of 9 parts of N-n-butyl-p-aminophenol and 1 part of N,N'-di-n-butyl-p-phenylene diamine (inhibitor base) was alkylated with acetaldehyde in the presence of hydrogen and Raney nickel. The reaction mixture was purified as in the preceding example and the effectiveness of the distilled dialkylated product consisting essentially of N-ethyl-N-n-butyl-p-aminophenol was determined. The results are set out in Table 4.

Table 4

Additive	Effective Inhibitor Ratio	Calculated Inhibitor Ratio
Inhibitor Base	1.00	----------
Distilled product	1.01	----------
1 part Base	1.065	1.005
1 part Distilled product		

Synergism is also apparent with blends containing N-methyl-N-n-butyl-p-aminophenol prepared by alkylating N-n-butyl-p-aminophenol with formaldehyde in the presence of hydrogen and Raney nickel.

Table 5

Additive	Effective Inhibitor Ratio	Calculated Inhibitor Ratio
N-n-butyl-p-aminophenol	1.00	----------
N-methyl-N-n-butyl-p-aminophenol	1.23	----------
1 part N-n-butyl-p-aminophenol	1.11	1.057
3 parts N-methyl-N-n-butyl-p-aminophenol		

In stabilizing motor fuels, the inhibitor blends of the invention can be used in amounts of from 0.001% to 0.1% or as high as 1%, although concentrations of 0.005% to 0.05% are usually preferred. They can be used alone or in combination with other additives such as metal deactivators, antiknock compounds, antirusts and the like. The inhibitors can be added to the gasoline with or without use of an auxiliary solvent, solutions in aliphatic alcohols such as isopropyl alcohol being preferred. In the case of the compositions containing N-n-butyl-N-isobutyl-p-aminophenol, isobutyl alcohol admixed with isopropyl alcohol is the preferred solvent both from the standpoint of gasoline solubility and solubility in the solvent. Solutions containing from about 50% to about 55% of the inhibitor blend in the solvent are preferred.

The reasons for the synergism between the monoalkylated and dialkylated inhibitors is not understood, and the invention is not limited thereby. Although the invention has been described in detail with reference to preferred embodiments thereof, variations and modifications can be effected within the spirit and scope of the invention as described hereinabove and as defined in the appended claims.

I claim:

1. Gasoline containing cracked stock having incorporated therein a stabilizing amount in the range of 0.001% to 1% by weight of a synergistic inhibitor composition consisting of a mixture of 1–90% by weight of N-n-butyl-N-isobutyl-p-aminophenol and 99–10% by weight of N-n-butyl-p-aminophenol, said composition including about 10% by weight of N,N'-di-n-butyl-p-phenylene diamine based on the weight of said N-n-butyl-p-aminophenol.

2. Gasoline containing cracked stock stabilized with 0.001% to 1% by weight of a synergistic inhibitor mixture of 25–35% by weight of N-n-butyl-N-isobutyl-p-aminophenol and 75–65% by weight of N-n-butyl-p-aminophenol, both based on the weight of said mixture.

3. Gasoline containing cracked stock having incorporated therein a stabilizing amount in the range of 0.005% to 0.05% by weight of an inhibitor composition of a mixture of 25–35% by weight of N-n-butyl-N-isobutyl-p-aminophenol and 75–65% by weight of N-n-butyl-p-aminophenol, both based on the weight of said mixture, said composition including about 10% by weight of N,N'-di-n-butyl-p-phenylene diamine based on the weight of N-n-butyl-p-aminophenol.

4. Gasoline containing cracked stock stabilized with 0.001% to 1% by weight of a synergistic inhibitor mixture of 1–90% by weight of N-n-butyl-N-isobutyl-p-aminophenol and 99–10% by weight of N-n-butyl-p-aminophenol, both based on the weight of said mixture.

5. Gasoline containing cracked stock stabilized with 0.001% to 1% by weight of a synergistic inhibitor composition consisting of 90–100% by weight of a mixture of 1–90% by weight of N-n-butyl-N-isobutyl-p-aminophenol and 99–10% by weight of N-n-butyl-p-aminophenol, and 10–0% by weight of N,N'-di-n-butyl-p-phenylene diamine.

6. A composition capable of synergistic inhibitor activity when incorporated in gasoline containing cracked stock, said composition being a mixture of 1–90% by weight of N-n-butyl-N-isobutyl-p-aminophenol and 99–10% by weight of N-n-butyl-p-aminophenol.

7. A composition capable of synergistic inhibitor activity when incorporated in gasoline containing cracked stock, said composition being a mixture of 1–90% by weight of N-n-butyl-N-isobutyl-p-aminophenol and 99–10% by weight of N-n-butyl-p-aminophenol, said composition including about 10% by weight of N,N'-di-n-butyl-p-phenylene diamine based on the weight of said N-n-butyl-p-aminophenol.

8. A composition capable of synergistic inhibitor activity when incorporated in gasoline containing cracked stock, said composition being a mixture of 25–35% by weight of N-n-butyl-N-isobutyl-p-aminophenol and 75–65% by weight of N-n-butyl-p-aminophenol.

9. A composition capable of synergistic inhibitor activity when incorporated in gasoline containing cracked stock, said composition consisting of about 10% by weight of a mixture of 25–35% by weight of N-n-butyl-N-isobutyl-p-aminophenol and 75–65% by weight of N-n-butyl-p-aminophenol, and about 10% by weight of N,N'-di-n-butyl-p-phenylene diamine based on the weight of said N-n-butyl-p-aminophenol.

10. A composition capable of synergistic inhibitor activity when incorporated in gasoline containing cracked stock, said composition consisting of 90–100% by weight of a mixture of 1–90% by weight of N-n-butyl-N-isobutyl-p-aminophenol and 99–10% by weight of N-n-butyl-p-aminophenol, and 10–0% by weight of N,N'-di-n-butyl-p-phenylene diamine based on the weight of said N-n-butyl-p-aminophenol.

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