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2,699,385

HYDROCARBON FUEL OIL COMPOSITIONS

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This invention relates to improved fuels for use in internal combustion engines of the diesel or compression ignition type, and for use in engines of the reaction type, such as ram-jet, turbo-jet engines and the like; more particularly, the invention concerns hydrocarbon fuel oil compositions having enhanced ignition characteristics.

In the manufacture of fuels for use in diesel type internal combustion engines and reaction type engines, it has been found that many of the petroleum oil fractions whose boiling range, viscosity, and other physical characteristics render them potentially suitable for such uses have improper combustion or ignition characteristics. In the case of diesel fuels, the unsatisfactory ignition qualities take the form of too great a time-lag between injection of the fuel into the cylinder and the spontaneous ignition thereof near the end of the compression stroke, with consequent knocking, smoking, and uneven running of the engine. The extent of the time-lag or ignition delay of a diesel fuel is conveniently evaluated by a determination of its so-called cetane number. In brief, the cetane number of a fuel may be defined as the per cent by volume of cetane in a blend of cetane and alphas-methylnaphthalene which has the same combustion characteristics as the fuel in question. A high cetane number indicates a low ignition delay period, and hence better performance as a diesel fuel. In the case of jet fuels, a similar problem is encountered in that a delay in ignition of the jet fuel upon injection of the fuel into the engine prevents optimum performance of the reaction engine. Thus an increase in the cetane number of a fuel corresponds to a decrease in the ignition delay period, which is desirable in both diesel fuel and jet fuel.

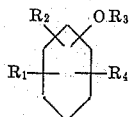
In view of the relatively low cetane numbers of many petroleum oil fractions which are otherwise suited for use as diesel fuels, it has been proposed to blend with such fractions additive materials which have the property of decreasing the ignition delay period, i. e. of increasing the cetane number of the fraction. Improvement of the ignition characteristics of jet fuels by various additives has similarly been proposed.

Accordingly, it is an object of this invention to provide hydrocarbon fuel oil compositions wherein the combustion characteristics of the fuel are improved without adversely altering other desirable properties of the fuel oil.

More specifically, it is an object of our invention to improve the cetane number of diesel fuel compositions.

A further object of our invention is to provide improved jet fuel compositions which exhibit a decreased ignition delay period compared with unimproved jet fuels.

These and other objects are accomplished by the present invention wherein we provide improved fuel compositions comprising a major amount of a hydrocarbon fuel oil and a minor amount, sufficient to increase appreciably the burning rate of the fuel, of a compound having the following structural formula:



wherein R₁, R₂ and R₃ are selected from alkyl, alkenyl groups and H, at least one of R₁, R₂ and R₃ being an alkenyl group, and R₄ is selected from the group consisting of H, OH, alkenoxy, and alkoxy groups, the double

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bond in each alkenyl and alkenoxy group being at least one carbon atom removed from the alpha carbon atom thereof.

The alkenyl derivatives of this class, wherein the alkenyl group contains from 3 to 5 carbon atoms, are preferred, particularly where R₁, R₂, R₃ are alkenyl and R₄ is alkenoxy. Illustrative of preferred alkenyl groups are allyl, butenyl, and 1,1-dimethylallyl. Thus, both straight and branched chain groups are suitable. It is also preferred to employ in the alkyl derivatives, alkyl groups containing from 1 to 18 carbon atoms. Methyl, ethyl, butyl, hexyl, octyl and decyl groups are illustrative. Both the alkenyl and alkyl groups may contain further substituents which do not adversely affect the oil solubility of the compound or its ignition promoting characteristics.

To further illustrate the type of compounds falling within the scope of the above generic formula, the following specific examples of compounds are presented:

- 20 Mono-allyl phenol
Diallyl phenol
Mono-allyl resorcinol
Diallyl hydroquinone
- 25 Hydroquinone mono-butenyl ether
Di-, 1-dimethylallyl ether of catechol
Butenyl ether of mono-allyl phenol
Mono-allyl ether of mono-butenyl resorcinol
Diallyl ether of monobutenyl catechol
Diallyl ether of diallyl catechol
- 30 Mono-butyl ether of mono-butenyl hydroquinone
Mono-butyl, mono-allyl ether of mono-allyl-resorcinol
Mono-butyl, mono-allyl ether of di-allyl catechol
2-methyl, 4-allyl phenol
Allyl ether of cresol
- 35 1, 1-dimethylallyl ether of 2-butenyl-4-tertiary butyl phenol
Mono-allyl ether 2-methyl-6-allyl catechol
Di-allyl ether of butylhydroquinone
Mono-methyl ether of 2-methyl-6-allyl-hydroquinone
- 40 Mono-butyl mono-allyl ether of butylcatechol
Mono-allyl ether of di-tertiarybutylcatechol
Di-allyl ether of di-tertiarybutylcatechol
Mono-methyl, mono-butenyl ether of dibutyl-hydroquinone
- 45 Methyl ether of butenylphenol
Ethyl ether of diallylphenol
Mono-butyl ether of butenylhydroquinone
Mono-methyl ether of di-1, 1-dimethylallylresorcinol
Mono-butyl, mono-butenyl ether of allylcatechol
- 50 Dibutyl ether of allylhydroquinone
Dimethyl ether of diallylcatechol
Ethyl ether of 2-methyl-4-allylphenol
Mono-butyl ether of 2-methyl-6-allyl-hydroquinone
Dimethyl ether of 4-allyl-6-ethylcatechol

The above compounds are prepared by methods well-known in the art. For example, the alkenyl derivatives can be prepared by alkylating a mono- or di-hydroxy phenol with alkenyl chlorides under controlled conditions. Depending upon the conditions employed, it is thus possible to obtain either nuclear substituted alkenyl-phenols, alkenylphenyl ethers, or both. By way of illustration, allyl phenols may be prepared by allylating phenols with allyl chloride to form the corresponding ethers, which may be employed as such; the ethers may also be rearranged to form the nuclear substituted allyl phenols. Alternatively, nuclear substituted allyl phenols may be prepared directly by allylation, followed by further allylation to produce allyl ethers of allyl phenols.

More specifically, allyl aryl ethers are usually prepared by refluxing a phenol with allyl bromide and anhydrous potassium carbonate for several hours in an acetone solution. Allyl bromide may be replaced by allyl chloride and sodium iodide, and acetone may be replaced by the higher boiling methyl ethyl ketone. This method usually gives good yields but is unsatisfactory for weakly acidic phenols, for which various modifications have been proposed. For example, such phenols may be treated with sodium ethoxide in ethanol solution, then with allyl halide.

The Williamson synthesis, using a sodium phenoxide

and allyl bromide in methanol solution, is more rapid than the procedure using acetone and potassium carbonate, and gives good results. Aqueous acetone also has been used as a reaction medium for the formation of allylethers of phenols by treatment of the phenol with sodium hydroxide and allyl halide. The following example, involving the preparation of the allyl ether of 4-octylphenol, is illustrative of such a procedure:

Example I.—To prepare 4-octylphenyl allyl ether, a mixture of 1.0 mol p-octylphenol, 1.0 mol sodium hydroxide, 300 ml. water, and 300 ml. acetone was made homogeneous by warming. Thereafter, 1.0 mol of allyl chloride was added slowly to the refluxing solution. When about three-fourths of the total allyl chloride had been added, the reaction mixture became cloudy. Refluxing was continued for sixteen hours. The organic layer was separated off, dissolved in petroleum ether, washed with water, dried and distilled at reduced pressure from a Claisen flask.

The following cuts were taken:

	Pressure, mm.	Temperature, ° C.	Weight, grams
(1)-----	0.8	100-112	81.1
(2)-----	0.8	110-114	91.6
(3)-----	0.8	110-117	44.6
(4)-----	0.8	119-137	10.3

Cuts No. 1, 2, and 3 (representing a total yield of 88.3% theoretical yield of 4-octylphenyl allyl ether) were analyzed for iodine number and acetyl number with the following results:

	Iodine No.	Acetyl No.
(1)-----	104.5	51.5
(2)-----	105.4	31.2
(3)-----	105.1	36.0
Theoretical values for 4-octylphenyl allyl ether-----	103	0
Theoretical values for 2-allyl-4-octylphenol-----	103	228

By treatment of cuts No. 2 and 3 with "Claisen's alkali," phenolic contaminants of the ether were removed and the pure product analyzed as follows:

Iodine No. =105.4, Acetyl No.=0

The simpler allyl aryl ethers can be rearranged by refluxing at atmospheric pressure until the boiling point becomes constant; since the boiling point of the product is higher than that of the ether, the boiling point rises until the reaction is complete.

Ethers of higher boiling point frequently undergo undesirable side reactions when refluxed at atmospheric pressure, and better yields may be obtained by refluxing at reduced pressure. A similar result may be more conveniently obtained by using a solvent to act as diluent, such as dimethylaniline or diethylaniline. A non-oxidizing atmosphere such as nitrogen is recommended.

The reaction mixture is usually worked up by removing the basic solvent, if present, with dilute mineral acid, solution of the residue in petroleum ether, and extraction with aqueous alkali to separate the phenolic product from any neutral byproducts and unchanged ether. When the phenols are highly substituted, their acidity may be so greatly diminished that they are practically insoluble in aqueous alkali. "Claisen's alkali" may be used then. Alkyl substituents in the α - or γ -position of the allyl group increase the rate of rearrangement. The preparation of 2-allyl-4-octylphenol by rearrangement of 4-octylphenyl allyl ether is illustrated by Example II.

Example II.—To 76.0 grams of 4-octylphenyl allyl ether (Iodine No. 104.5; Acetyl No. 51.5) were added 38.0 grams of diethylaniline. The solution was heated at 223-250° C. in a nitrogen atmosphere for about 5½ hours. The reaction mixture was dissolved in petroleum ether, then extracted with cold dilute sulfuric acid to remove diethylaniline. The remaining ether solution was extracted several times with Claisen's alkali. The alkaline extract was diluted with water, acidified with dilute hydrochloric acid and extracted with petroleum ether. The ether solution was washed with distilled water until neutral and dried to constant weight. Product yield obtained was 68.6 grams or 90.2% of theory based on the starting

weight of 4-octylphenyl allyl ether. Iodine No.=100; Acetyl No.=202.3. Theory for 2-allyl-4-octylphenol; Iodine No.=103, Acetyl No.=228. Further purification of this product was not attempted.

By suitable modification, the general procedure for the preparation of allyl ethers from phenols and their rearrangement to allyl phenols, as discussed supra, can be used for the preparation of the compounds listed hereinabove. As pointed out, nuclear substituted alkenyl phenols can also be prepared by direct C-alkenylation of the sodium salt of the phenol in benzene solution. In general, this method is not as effective for the preparation of allyl phenols as is the preparation of the allyl ether followed by rearrangement, because a mixture of products is obtained in C-alkenylation. However, by employing the procedure outlined in U. S. Patent 2,459,835 to Monroe, direct nuclear allylation of dihydroxybenzenes occurs in good yield. Further allylation produces allyl ethers of allyl dihydroxybenzenes. As shown therein, the diallyldihydroxybenzene is formed by the nuclear alkenylation of the dihydroxybenzene with allyl halides, particularly allyl chloride. The pH of the aqueous reaction mixture should be maintained between 5 and 7 for maximum yield. Since the allylation reaction is exothermic, it is also necessary to maintain a low temperature, such as from 42° to 45° C., to avoid polymerization and secondary reactions. In addition, because hydrochloric acid is formed by the reaction, the allyl chloride is added to the dihydroxybenzene in a series of fractional portions and, prior to the addition of the allyl chloride, a base solution, such as sodium hydroxide, is introduced into the reaction mixture to neutralize the hydrochloric acid as formed. Furthermore, it is important that the dihydroxybenzene be dissolved in a buffer solution, such as sodium acid phosphate, the buffer acting to maintain the reaction solution pH between 5 and 7. Further allylation of the diallylcatechol thus prepared, with allyl chloride under similar conditions, except that the pH of the buffered system is held at 7 or above, will result in the formation of the diallyl ether of diallylcatechol.

The aforesaid procedure or obvious modifications thereof can be employed advantageously for the preparation of such compounds as the following:

- 45 Monoallyl resorcinol
- Diallylhydroquinone
- Monoallyl ether of monobutenylresorcinol
- Diallyl ether of monobutenylcatechol
- 50 Diallyl ether of diallylcatechol
- Monobutyl ether of monobutenylhydroquinone
- Monobutyl monoallyl ether of monoallylresorcinol
- Monobutyl monoallyl ether of diallylcatechol
- Monoallyl ether of 3-methyl-6-allylhydroquinone
- 55 Monomethyl ether of 2-methyl-6-allylhydroquinone
- Monobutyl ether of butenylhydroquinone
- Monomethyl ether of di-1,1-dimethylallylresorcinol
- Monobutyl monobutenyl ether of allylcatechol
- 60 Dibutyl ether of allylhydroquinone
- Dimethyl ether of diallylcatechol
- Monobutyl ether of 2-methyl-6-allylhydroquinone
- Dimethyl ether of 4-allyl-6-ethylcatechol

Whether alkylation precedes alkenylation depends on which is more expedient for the particular preparation at hand.

The alkyl derivatives in turn are prepared by controlled alkylation with alkyl halides. They may also be prepared by alkylation with olefins in the presence of a condensation catalyst, such as concentrated sulfuric acid. Suitable alkylating agents include ethylene, butene-1, isobutylene, the amylene, di-isobutylene, tri-isobutylene, and hexene.

A wide variety of diesel fuels and jet fuels are benefited by the class of compounds employed in accordance with our invention. The designation of these fuels as "hydrocarbon fuel oils" is intended to include both types of fuels. Thus the hydrocarbon fuels of our invention include fuels boiling in the range of 300 to 800° F. These fuels in turn may be prepared from gas oils, residual oils, recycle stocks, shale oils, coal tar oils, hydrogenated petroleum and coal tar oils, and various paraffinic, naphthenic or asphaltic base distillates, as well as synthetic hydrocarbon oils such as those produced by the Fischer-Tropsch synthesis. In accordance with cus-

tomary practice, the base fuel is usually blended from several types of stock to adapt it to a particular type of engine and specific operating conditions. As illustrative of suitable diesel fuels, the inspection data for several typical diesel fuels are set forth hereinafter in Table I.

TABLE I
Typical diesel fuels

	Penn Gas Oil	No. 2 Furnace Oil	Medium Diesel Oil	Heavy Diesel Oil
Gravity, ° API.....	43	33	25	23
Vis. (Saybolt at 100° F.).....	35	36	100	172
Diesel Index.....	74	41	43.3	41
Cetane No.....	60+	49	43.6	40.9
Over.....	380	358	376	407
10%.....	441	426	504	514
50%.....	494	492	796	697
90%.....	573	593	906 (80%)	713 (60%)
End.....	630	645		

As further illustrative of suitable fuels for use in accordance with our invention, the inspection data for a typical jet fuel is set forth in Table II. This fuel is essentially kerosene boiling range material. Jet engines, however, can utilize a considerable wider range of materials, both higher and lower boiling.

TABLE II
Inspection data on jet fuel

Gravity, ° API.....	36.5
ASTM distillation:	
IBP, ° F.....	320
5% recovered at, ° F.....	342
10% recovered at, ° F.....	350
50% recovered at, ° F.....	380
90% recovered at, ° F.....	422
End point, ° F.....	468
Per cent recovered.....	98.5
Per cent residue.....	1.5
Per cent loss.....	0.0
Color, Saybolt.....	+16
Acid heat, ° F.....	1
Freezing point, ° F.....	< -76
Accelerated Ginn test mg./100 ml.....	2.5
Glass dish Ginn mg./100 ml.....	0.2
Copper strip corrosion, 3 hr. at 212° F.....	Pass
Flash point, TCC, ° F.....	116
Vis. at 100° F. centistokes.....	1.48

The fuel oil compositions of our invention may be prepared simply by blending the additive into the fuel base in the desired proportions. Alternatively, in some instances it may be more convenient to prepare a concentrate of the additive in the fuel base, and thereafter blend the concentrate with a further quantity of the same or a different fuel base to secure the desired composition. In general, relatively minor amounts of the compounds set forth, such as from 0.01 to 10 per cent by weight of the fuel oil composition, are sufficient to increase appreciably the burning rate of the fuel.

Example III.—The effectiveness of the herein-described class of compounds in improving the ignition characteristics of a typical diesel fuel is illustrated by the following data in Table III, obtained by determining the cetane number of an Eastern Venezuela straight-run fuel oil containing varying amounts of the allyl ether of 4-octylphenol prepared in accordance with Example I.

TABLE III

Fuel Composition	Cetane Number	Cetane Number Increase
Eastern Venezuela straight-run fuel oil.....	45.7	-----
+3% (wt.) allyl ether of 4-octylphenol.....	47.3	1.6
+6% (wt.) allyl ether of 4-octylphenol.....	47.0	1.3

Example IV.—The results of similar tests conducted on an Eastern Venezuela straight-run fuel oil containing three per cent of the 2-allyl-4-octylphenol prepared in accordance with Example II are set forth hereinafter in Table IV.

TABLE IV

Fuel Composition	Cetane Number	Cetane Number Increase
Eastern Venezuela straight-run fuel oil.....	45.7	-----
+3% (wt.) 2-allyl-4-octylphenol.....	46.7	1.0

Example V.—The results of further tests on a typical diesel fuel are illustrated by the following data in Table V, obtained by determining the cetane number of a cracked diesel fuel containing varying amounts of diallylhydroquinone.

TABLE V

Fuel Composition	Cetane Number	Cetane Number Increase
Light recycle FCC fuel oil distillate.....	29.3	-----
+1% (wt.) diallylhydroquinone.....	29.6	0.3
+3% (wt.) diallylhydroquinone.....	31.0	1.7

Example VI.—The results of similar tests conducted on a straight-run diesel fuel containing varying amounts of diallylcatechol are set forth hereinafter in Table VI:

TABLE VI

Fuel Composition	Cetane Number	Cetane Number Increase
Eastern Venezuela straight-run fuel oil.....	47.7	-----
+1.0% (wt.) of diallylcatechol.....	49.1	1.4
+3.0% (wt.) of diallylcatechol.....	49.8	2.1

Example VII.—Other tests conducted on a straight-run diesel fuel oil containing varying amounts of diallyl ether of diallylcatechol further indicate the effectiveness of the ether derivatives as shown by the test data in Table VII:

TABLE VII

Fuel Composition	Cetane Number	Cetane Number Increase
Eastern Venezuela straight-run fuel oil.....	46.0	-----
+1.0% (wt.) of diallyl ether of diallylcatechol.....	51.4	5.4
+3.0% (wt.) of diallyl ether of diallylcatechol.....	53.1	7.3
+5.0% (wt.) diallyl ether of diallylcatechol.....	54.7	8.7

It is readily seen that the diallylcatechol tested in Example VI was more effective than the compounds tested in Examples III, IV and V. Moreover, the diallyl ether of diallylcatechol, tested in Example VII, was considerably more effective than any of the other compounds in the illustrative examples for improving the cetane number of the base fuel. The effect produced by these compounds is surprising in view of the fact that cetane improvers are generally compounds rich in oxygen or in a highly oxidized condition, such as peroxides, polysulphides, nitro and nitroso compounds, nitriles and the like.

Thus it is evident that the employment of the class of compounds set forth in accordance with our invention results in hydrocarbon fuels characterized by increased burning rates or reduced ignition delay periods, such that important advantages may be obtained therefrom. These advantages include the alleviation of knocking and smoking problems, more even running of engines, cleaner and more complete combustion of the fuel, and general improvement of fuel oil ignition characteristics.

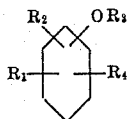
The improved fuel oil compositions provided by our invention may contain any of the agents commonly employed to enhance other properties of such fuels. For example, they may contain corrosion inhibitors, antioxidants, oiliness agents, detergents or dispersing agents, gum solvents, viscosity improvers, fuel oil stabilizers and the like. The class of compounds employed in accordance with our invention functions effectively in the presence of such agents.

Resort may be had to such modifications and varia-

tions as fall within the spirit of the invention and the scope of the appended claims.

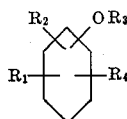
What we claim is:

1. An improved fuel composition comprising a major amount of a hydrocarbon fuel oil and a minor amount, sufficient to increase appreciably the burning rate of the fuel, of a compound having the following structural formula:



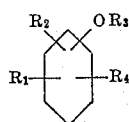
wherein R₁, R₂ and R₃ are selected from the group consisting of alkyl, alkenyl groups and H, at least one of R₁, R₂ and R₃ being an alkenyl group, and R₄ is selected from the group consisting of H, OH, alkenoxy and alkoxy groups, the double bond in each alkenyl and alkenoxy group being at least one carbon atom removed from the alpha carbon atom thereof.

2. An improved fuel composition comprising a major amount of a hydrocarbon fuel oil and a minor amount, sufficient to decrease appreciably the ignition delay period of the fuel, of a compound having the following structural formula:



wherein R₁, R₂ and R₃ are selected from the group consisting of alkyl, alkenyl groups, and H, at least one of R₁, R₂ and R₃ being an alkenyl group, and R₄ is selected from the group consisting of H, OH, alkenoxy and alkoxy groups, said alkenyl and alkenoxy groups containing from 3 to 5 carbon atoms arranged such that the double bond in each group is at least one carbon atom removed from the alpha carbon atom thereof, and said alkyl and alkoxy groups containing from 1 to 18 carbon atoms.

3. An improved fuel composition comprising a major amount of a hydrocarbon fuel oil and about 0.01 to 10 per cent by weight of the composition of a compound having the following structural formula:



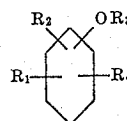
wherein R₁, and R₂ and R₃ are selected from the group consisting of alkyl, alkenyl groups, and H, at least one of R₁, R₂ and R₃ being an alkenyl group, and R₄ is selected from the group consisting of H, OH, alkenoxy and alkoxy groups, said alkenyl and alkenoxy groups containing from 3 to 5 carbon atoms arranged such that the double bond in each group is at least one carbon atom removed from the alpha carbon atom thereof, and said alkyl and alkoxy groups containing from 1 to 18 carbon atoms.

4. The composition of claim 1 wherein R₁ and R₂ are alkenyl, R₃ is H, and R₄ is OH.

5. The composition of claim 1 wherein R₁, R₂ and R₃ are alkenyl, and R₄ is alkenoxy.

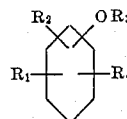
6. An improved fuel composition comprising a major amount of a hydrocarbon fuel oil and a minor amount, sufficient to increase appreciably the burning rate of the

fuel, of a compound having the following structural formula:



wherein R₁ is alkyl, R₂ is H, R₃ is an alkenyl group, the double bond of which is at least one carbon atom removed from the alpha carbon atom of said group, and R₄ is H.

7. An improved fuel composition comprising a major amount of a hydrocarbon fuel oil and a minor amount, sufficient to increase appreciably the burning rate of the fuel, of a compound having the following structural formula:



wherein R₁ is alkyl, R₂ is an alkenyl group, the double bond of which is at least one carbon atom removed from the alpha carbon atom of said group, and R₃ and R₄ are H.

8. An improved fuel composition comprising a major amount of a hydrocarbon fuel oil and a minor amount, sufficient to increase appreciably the burning rate of the fuel, of diallyl catechol.

9. An improved fuel composition comprising a major amount of a hydrocarbon fuel oil and a minor amount, sufficient to increase appreciably the burning rate of the fuel, of diallyl hydroquinone.

10. An improved fuel composition comprising a major amount of a hydrocarbon fuel oil and a minor amount, sufficient to increase appreciably the burning rate of the fuel, of diallyl ether of diallyl catechol.

11. An improved fuel composition comprising a major amount of a hydrocarbon fuel oil and a minor amount, sufficient to increase appreciably the burning rate of the fuel, of the allyl ether of 4-octylphenol.

12. An improved fuel composition comprising a major amount of a hydrocarbon fuel oil and a minor amount, sufficient to increase appreciably the burning rate of the fuel, of 2-allyl-4-octylphenol.

13. The composition of claim 8 wherein the diallyl catechol is present in an amount of from about 0.01 to 10 per cent by weight of the composition.

14. The composition of claim 9 wherein the diallyl hydroquinone is present in an amount of from about 0.01 to 10 per cent by weight of the composition.

15. The composition of claim 10 wherein the diallyl ether of diallyl catechol is present in an amount of from about 0.01 to 10 per cent by weight of the composition.

16. The composition of claim 11 wherein the allyl ether of 4-octylphenol is present in an amount of from about 0.01 to 10 per cent by weight of the composition.

17. The composition of claim 12 wherein the 2-allyl-4-octylphenol is present in an amount of from about 0.01 to 10 per cent by weight of the composition.

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