June 7, 1966 B. E. MARSH ETAL 3,254,974

STABILIZED FUEL OIL COMPOSITIONS

Filed April 20, 1962 3 Sheets-Sheet 1

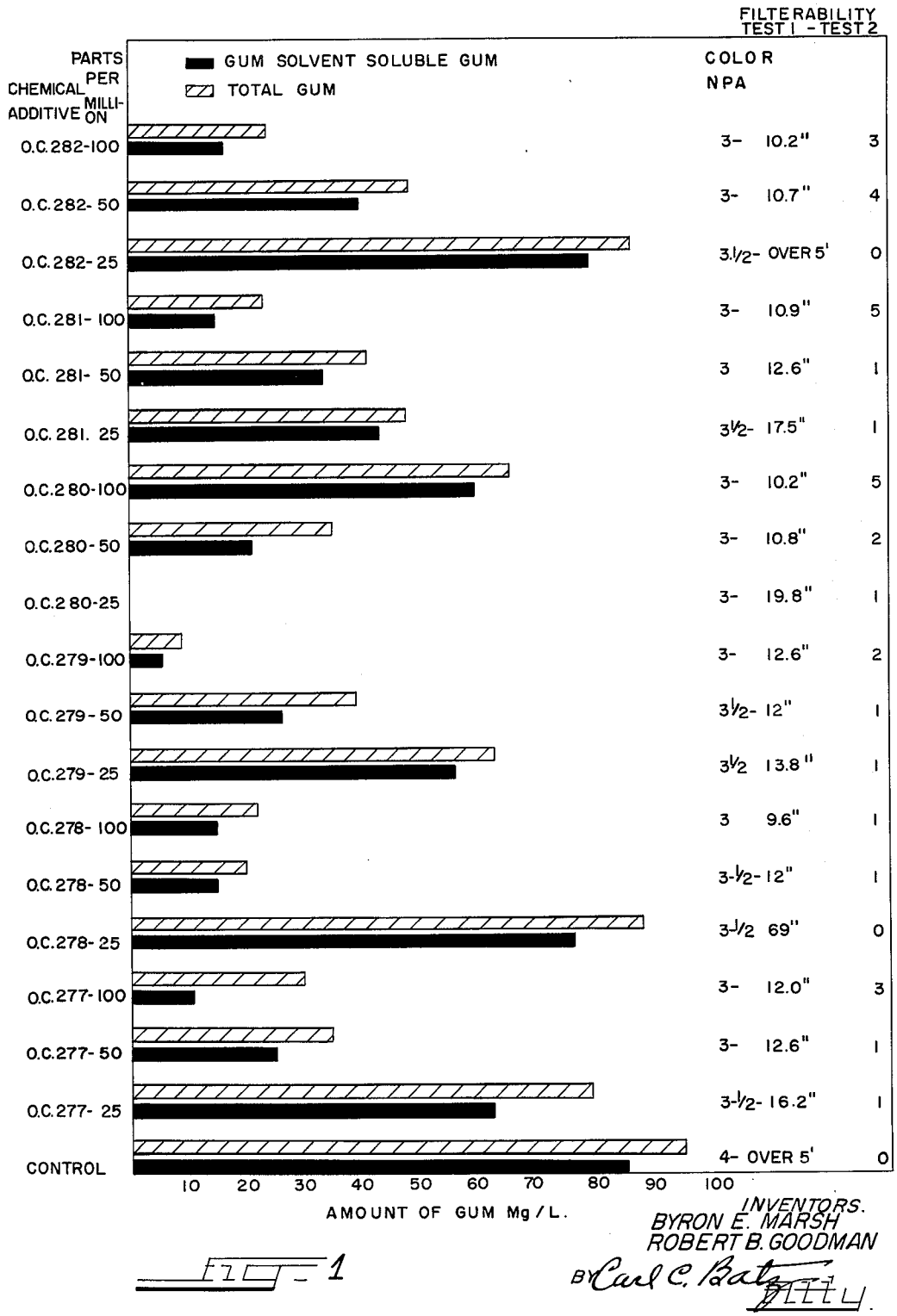


Fig. 1

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STABILIZED FUEL OIL COMPOSITIONS

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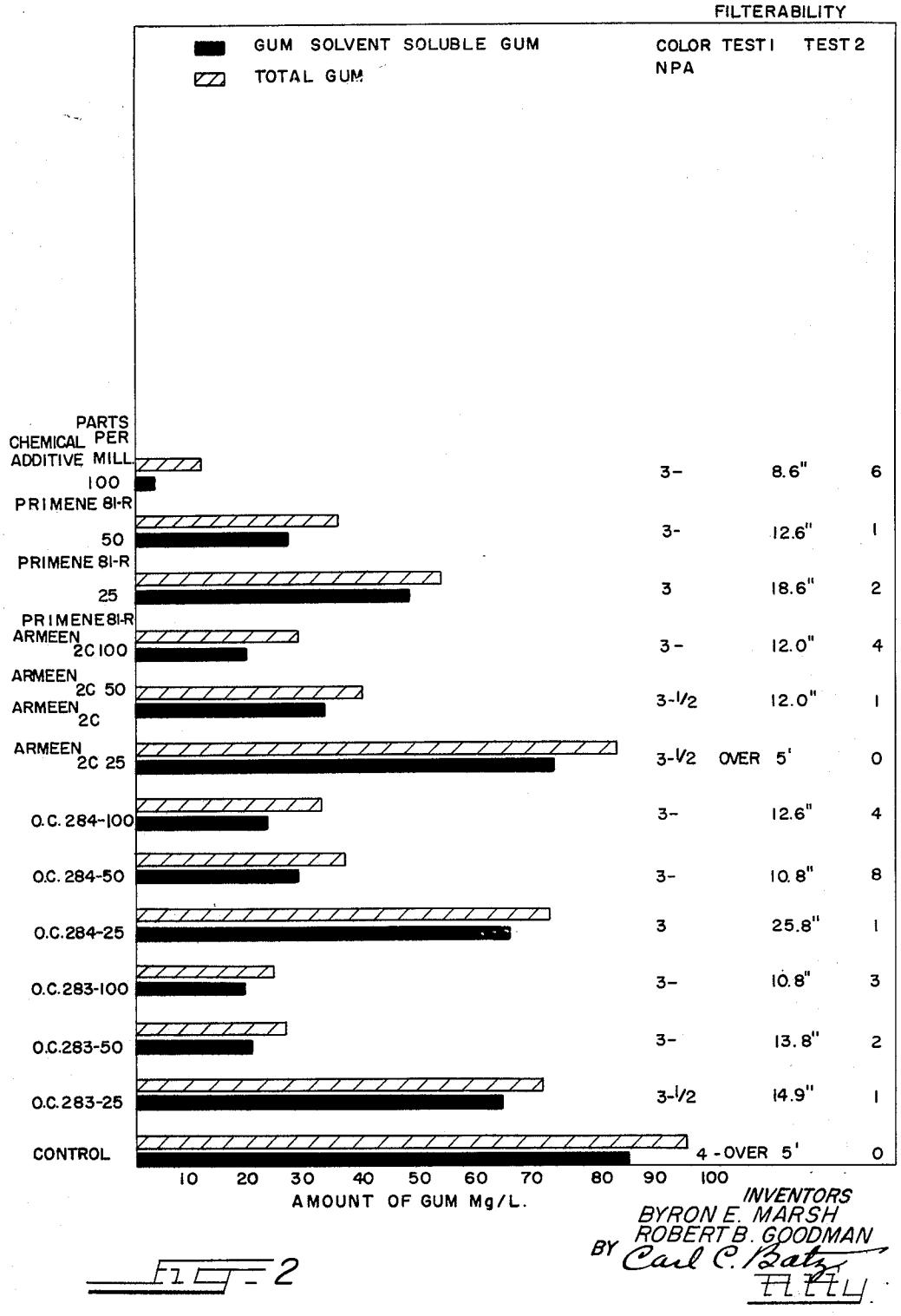


FIG. 2

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Filed April 20, 1962 3 Sheets-Sheet 3

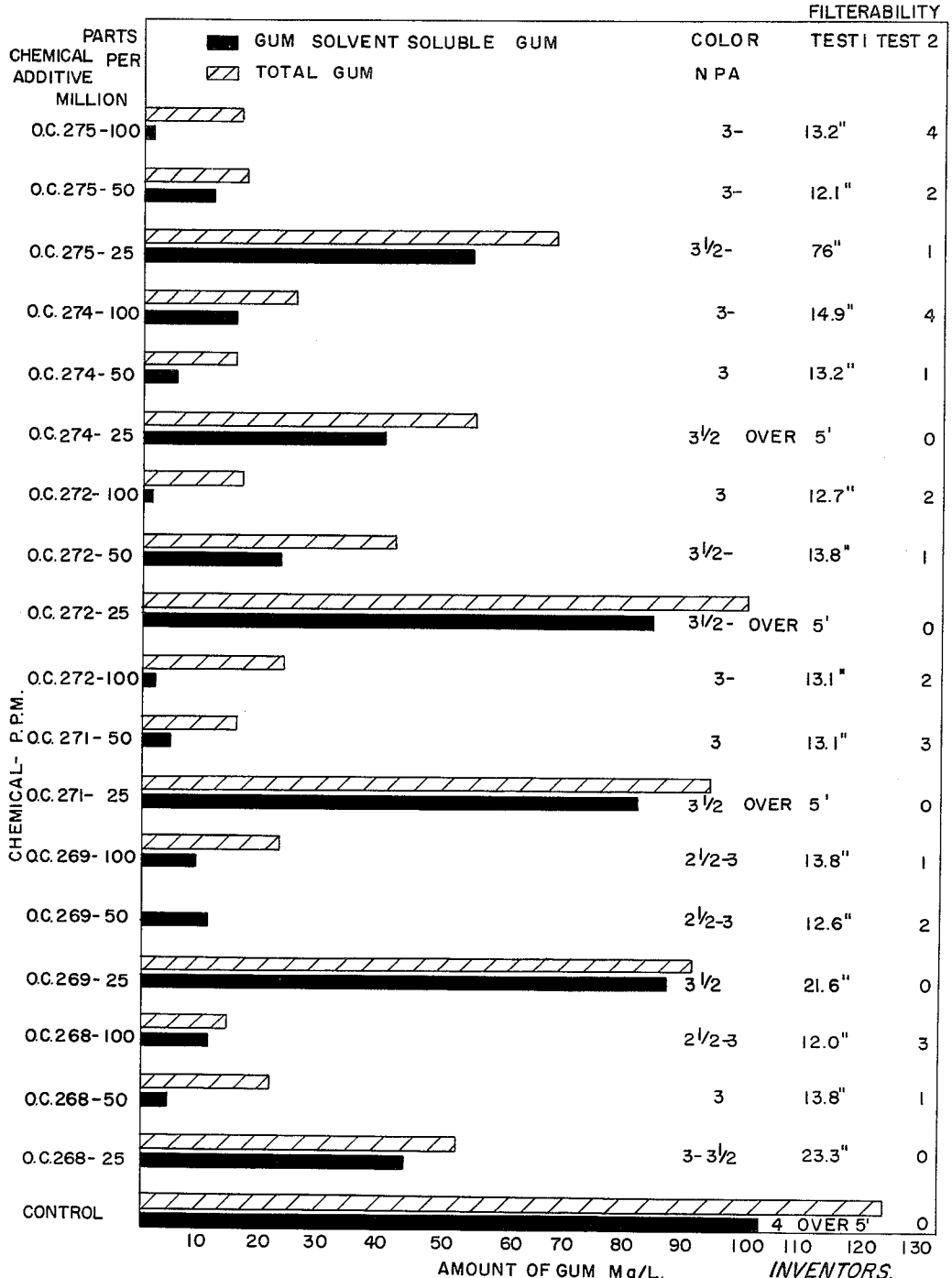


FIG. 3

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STABILIZED FUEL OIL COMPOSITIONS

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Filed Apr. 20, 1962, Ser. No. 188,966
7 Claims. (Cl. 44—72)

This invention relates to fuel oil compositions, and more particularly to a fuel oil composition in which sludging or clogging tendencies are inhibited.

The active chemical ingredient of this invention may be preferably dispersed or dissolved in treated or untreated cracked fuel oils or mixtures of cracked fuels with straight run fuel oils, said fuel oils having components normally distilling from about 300° F. to about 700° F. Preferred fuels have a boiling range of from about 340° F. to about 700° F., and particularly from about 400° F. to about 675° F. Specifically, hydrocarbon distillates which are utilized as bases in the compositions of this invention are cracked gas oils, fuel oils, furnace oils, burner oils, diesel fuel oils, kerosene, etc., and mixtures of said cracked fuels with the corresponding or like straight run hydrocarbon fractions.

Symmetrical secondary amines are not generally used as stabilizers for fuel oils because they are high-melting solids and require special handling and have other known disadvantages. We have discovered that unsymmetrical secondary amines may be effectively employed as stabilizers against gum or sludge formation and color degradation, while at the same time being generally liquid at room temperature. Other important advantages of the use of unsymmetrical secondary amines will appear hereinafter.

The primary object, therefore, is to provide an improved fuel oil containing unsymmetrical secondary amines and in which the latter serve as a stabilizer against gum or sludge formation and color degradation. A further object is to provide a heating oil or fuel oil composition in which unsymmetrical secondary amines which are generally liquid at room temperature are employed for stabilizing the oils against sludging, etc. Yet another object is to provide as a fuel oil additive to prevent sludging, etc., an unsymmetrical secondary amine prepared by reacting a primary fatty amine with a ketone or keto-ether to form a Schiff's base which is hydrogenated to produce an unsymmetrical secondary amine having a straight chain hydrocarbon radical and a branched chain hydrocarbon radical. A still further object is to prepare unsymmetrical amines by the reaction between long chain ketones and short chain amines, or between long chain amines and aldehydes. Other specific objects and advantages will appear as the specifications proceeds.

In one embodiment of our invention, we prepare for incorporation in a fuel oil an unsymmetrical secondary amine which may be prepared by reacting a primary fatty amine with a ketone or keto-ether to form a Schiff's base which is then hydrogenated to produce an unsymmetrical secondary amine having a straight chain hydrocarbon radical and a branched chain hydrocarbon radical. When a keto-ether is employed in the reaction, the branched chain will also contain an ether linkage.

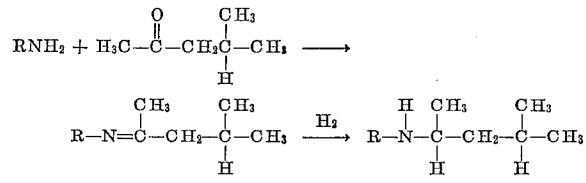
An unsymmetrical secondary amine product has the following molecular configuration:



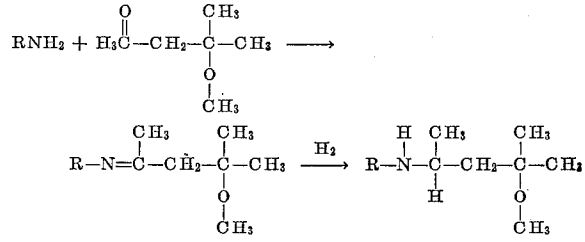
wherein R is a straight chain aliphatic hydrocarbon group having from 8 to 22 carbon atoms, and R′ is a branched chain aliphatic group having from 3 to 22 carbon atoms which may have the carbon chain interrupted by an ether linkage.

Specific examples of class of compounds may be set out as follows:

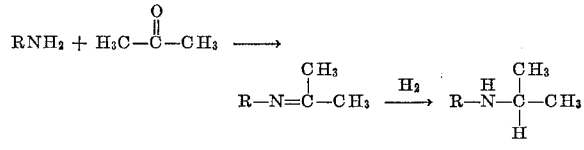
(1) Reaction products of fatty primary amines with methylisobutyl ketone.



(2) Reaction products of fatty primary amines with pent-oxone (a keto ether).



(3) Reaction products of fatty primary amines with acetone.



Illustrative of the first type were:

N 1,3-dimethylbutylstearylamine
N 1,3-dimethylbutyloleylamine
N 1,3-dimethylbutylcocoamine
N 1,3-dimethylbutyl hydrogenated tallow amine

Illustrative of the second type were:

N 1,3-dimethyl-3-methoxybutylcocoamine
N 1,3-dimethyl-3-methoxybutyl hydrogenated tallow amine
N 1,3-dimethyl-3-methoxybutylstearylamine

Illustrative of the third type was isopropylstearylamine,

If desired, in place of the primary amine reactant an N-substituted polyalkylene polyamine having at least one primary amino group could be used to prepare the unsymmetrical secondary amines. An example of this would be the reaction between Duomeen HT (N-hydrogenated-tallow trimethylene diamine) and methylisobutylketone with subsequent reduction of the Schiff's base.

The unsymmetrical secondary amine may be mixed with fuel oil in varying proportions depending upon the specific use of the fuel oil. Generally, we find that the unsymmetrical secondary amine may be mixed in the proportion of approximately 10–200 parts per million, with best results being obtained when the unsymmetrical secondary amine comprises 50–100 p.p.m.

Specific examples illustrative of the invention may be set out as follows:

EXAMPLE I

The following unsymmetrical secondary amines, which are liquid or readily formulated into liquid products, which is not true of our symmetrical secondary amines, were evaluated as fuel oil additives:

O.C. #267 N 1,3 dimethyl-3-methoxybutylidene cocoamine
O.C. #268 N 1,3 dimethyl-3-methoxybutyl cocoamine (crude)

O.C. #269 N 1,3 dimethyl-3-methoxybutyl cocoamine (distilled)
O.C. #270 N 1,3 dimethyl-3-methoxylbutylidene tallow amine
O.C. #271 N 1,3 dimethyl-3-methoxybutyl H tallow amine (crude)
O.C. #272 N 1,3 dimethyl-3-methoxybutyl H tallow amine (distilled)
O.C. #273 N 1,3 dimethyl-3-methoxybutylidene oleylamine
O.C. #274 N 1,3 dimethyl-3-methoxybutyl stearylamine (crude)
O.C. #275 N 1,3 dimethyl-3-methoxybutyl stearylamine (distilled)
O.C. #276 N 1,3 dimethylbutylidene oleylamine
O.C. #277 N 1,3 dimethylbutyl stearylamine (crude)
O.C. #278 N 1,3 dimethylbutyl oleylamine (crude)
O.C. #279 N 1,3 dimethylbutyl stearylamine (distilled)
O.C. #280 N 1,3 dimethylbutyl cocoamine (crude)
O.C. #281 N 1,3 dimethylbutyl cooamine (distilled)
O.C. #282 N 1,3 dimethylbutyl hydrogenated tallow amine (crude)
O.C. #283 N 1,3 dimethylbutyl hydrogenated tallow amine (distilled)
O.C. #284 Isopropylstearylamine (distilled)

Storage conditions were 110° F. for 13 weeks.

FIGURES 1, 2, and 3 show the values for gum solvent soluble gum, total gun, filterability, and color.

Test procedures

Gum determination.— 300 ml. samples of aged oil in bottles were filtered through tared F frit gooch crucibles under vacuum. The bottles and crucibles were washed free of oil with n-hexane. The soluble gum determination was made by solubilizing the plated gum (adhering to the bottle) and that retained by the crucible with gum solvent (50% acetone, 50% methanol). This solution was evaporated, dried to constant weight, and calculated as milligrams per liter. Total gum includes that which was soluble in gum solvent and that portion retained by the gooch crucible which was not soluble in gum solvent. It is also expressed as milligrams per liter.

Filterability.—Filtering characteristics after aging were determined by the du Pont test method using the following two procedures:

(1) Measure the time for 400 ml. of oil to flow through 1 cm.^{2} area of 400 mesh screen under a constant twelve inch head.

(2) Measure the number of 25 ml. increments that will flow through #4 Whatman filter paper under a constant twelve inch head. The test is terminated when less than 25 ml. flow through the filter in 20 minutes.

Color.—Color is determined by use of a NPA color wheel in a Hellige comparator.

In the foregoing tests, the source of fuel oil was the Pure Oil Company #2 furnace oil. Fourteen unsymmetrical secondary amines and four Schiff's bases were evaluated as stabilizers under storage conditions of 110° F. for 13 weeks. Armeen 2C (di-coco amine) and Primene 81R (mixture of tertiary alkyl primary amines, principally $C_{12}H_{25}NH_2$ to $C_{14}H_{29}NH_2$) were used as standards. Soluble and insoluble gum, filtering rates, and color degradation were determined on the samples at the end of the storage period using standard procedures.

All of the unsymmetrical secondary amines effectively stabilized the fuel oil. The Schiff's bases, which are the intermediate in the preparation of the amines, accelerated degradation of the fuel oil. N 1,3 dimethylbutyloleylamine and N 1,3 dimethyl-3-methoxybutylcocoamine were particularly effective as stabilizers in heating oil.

While in the foregoing specification we have set forth the composition and procedure for forming the same in considerable detail for the purpose of illustrating the invention, it will be understood that such detail or details may be varied widely by those skilled in the art without departing from the spirit of our invention.

We claim:

1. A hydrocarbon fuel oil composition consisting essentially of fuel oil normally subject to the formation of gums, and an effective quantity sufficient to stabilize said oil against gum formation of an unsymmetrical secondary amine having a straight chain hydrocarbon radical containing from about 8 to 22 carbon atoms and a branched chain hydrocarbon radical containing from about 3 to 22 carbon atoms.

2. A hydrocarbon fuel oil composition consisting essentially of fuel oil normally subject to the formation of gums, and about 10 to 200 parts per million of an unsymmetrical secondary amine having the following structure:



wherein R is a straight chain aliphatic hydrocarbon group having from 8 to 22 carbon atoms, and R' is selected from the group consisting of a branched chain aliphatic hydrocarbon group having from 3 to 22 carbon atoms and a branched chain aliphatic group containing from about 3 to 22 carbon atoms having an ether linkage within said chain.

3. The composition of claim 2 in which the unsymmetrical secondary amine is substantially liquid at room temperature.

4. The composition of claim 1 in which the fuel oil is heating oil.

5. A hydrocarbon fuel oil composition consisting essentially of fuel oil and about 10 to 200 parts per million N 1,3 dimethylbutyloleylamine.

6. A hydrocarbon fuel oil composition consisting essentially of fuel oil and about 10 to 200 parts per million of N 1,3-dimethyl-3-methoxybutylcocoamine.

7. A hydrocarbon fuel oil composition consisting essentially of fuel oil normally subject to the formation of gums, and an effective quantity sufficient to stabilize said oil against gum formation of an unsymmetrical secondary amine having a straight chain hydrocarbon radical containing from about 8 to 22 carbon atoms, and a branched chain aliphatic radical containing from about 3 to 22 carbon atoms having an ether linkage within said chain.

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