

CHEMICAL BASIS OF DIESEL FUEL STABILIZATION BY TERTIARY ALKYL PRIMARY AMINES

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ABSTRACT

The oxidative degradation products, formed under both the prolonged storage and thermal stress, are a problem in the utilization of diesel fuels. There is a continued challenge in developing fuel stabilizers that are increasingly cost-effective, do not degrade the performance of fuel, and are environmentally acceptable. Our interest in highly branched tertiary alkyl primary amines (TAPA) has led to evidence that they are excellent stabilizers for diesel fuels. TAPA possess unique chemical and physical properties. We will present the results of stability experiments for thermal and oxidative degradation of several diesel fuels. The TAPA are evaluated in these stability tests in comparison with other well-known stabilizers. Chemical factors preventing formation of color, insoluble sediments and gums were studied by modeling generally accepted degradation mechanisms. In this paper we will report our mechanistic investigation into the chemical details of the stabilization and effect of the TAPA chemical structure on the activity. Data for acid scavenging, reduction of hydroperoxides, and solubilization/dispersancy mechanisms of stabilization is presented

INTRODUCTION

The oxidative degradation products, formed under both the prolonged storage and thermal stress, continue to be a problem in the utilization of diesel fuels. Fuel-instability reactions are defined in terms of the formation of deleterious products, such as filterable sediment, adherent gums, and peroxides. Sediments and gums which result from the oxidation reactions act to block filters and deposit on surfaces. There may be a relationship between the chemistry of deposit formation during normal long term storage and the deposits obtained by thermal stressing. Fuels containing higher amounts of olefins, certain nitrogen and sulfur compounds, organic acids, or dissolved metals are likely to degrade more and faster. Insolubles in diesel fuels are known to occur through several generally agreed mechanisms¹. The sediment and gum formation mechanisms have been studied in great details^{2,3} and can be summarized as: acid-base reactions involving N, O, and S species, free radical induced polymerization reactions involving unsaturated hydrocarbons, and esterification reactions involving aromatic and heterocyclic species. Previous studies have indicated that certain sulfonic acids⁴, organic nitrogen compounds⁵, and olefins⁶, when added to fuels that are then subjected to thermal or oxidative stress, tend to produce insoluble sediments.

Stabilizing additives are often used to counteract the above mechanisms⁷. Several chemistries may contribute to fuel stabilization. Antioxidants act to inhibit the reactions that form sediment. Most additives control peroxide formation, but do not curb formation of polymerized gum products. Dispersants act to suspend any sediment particles that form and prevent them from agglomerating and becoming a problem. The stability enhancing additives for middle distillate fuels include hindered phenols, alkylated diphenylamines, phenylenediamines, tertiary amines, metal deactivators and dispersants. Amine additives are generally considered as antioxidants (aromatic amines) and to neutralize acidic impurities/by-products (tertiary amines). Tertiary amines are generally considered² better than secondary or primary amines as fuel antioxidants. Phenylenediamine type antioxidants are more effective than hindered phenols in neutralizing peroxides. It was found that traditional amine stabilizers fail to control peroxide formation adequately. Also, these amines, while being more effective than hindered phenols in gasoline, are not being used in diesel because they degrade distillate fuel stability^{2b}. Recent work has implicated that widely used fuel stabilizers such as hindered phenols are ineffective in reducing sediment formation. Phenylenediamines have been shown to be detrimental in both high and low sulfur diesels, as they participate in side reactions forming sediments^{2a} and increasing color body formation^{2c}. Thus, a search for better stabilizers continues.

Primary amines are not considered as good radical or peroxide quenchers as secondary or tertiary amines. This is true for typical straight-chain fatty amines. However, we are mainly interested⁷ in a special class of primary amines that possess branched alkyl chains with the primary amino group attached to a tertiary carbon⁸. We will refer to these as tertiary alkyl primary amines (TAPA). Branched tertiary alkyl primary amines possess excellent oil solubility⁷, superior

thermal and oxidative stability¹⁰, strong basicity, and fluidity over a wide temperature range (See Table I). These benefits find usage in lubricant applications¹¹ also. We have previously shown¹² that TAPA can be used as fuel stabilizers, and are better than several other common stabilizers. We will describe here the work carried out recently at Rohm and Haas research laboratories with TAPA for their ability to stabilize diesel fuels. An attempt is made to form an interpretation of stabilization mechanisms of TAPA by using stability test methods under various conditions.

EXPERIMENTAL

I. Fuel Samples And Additives: Fresh test samples of diesel fuel without any additives were obtained from commercial sources. The fuel samples were analyzed to ensure conformance with specifications and stored under ambient temperature, in dark, and under nitrogen atmosphere. All tests were started within a month of obtaining the fresh samples. All commercial additives used were as received without further purification. All the C₉, C₁₂, and C₁₈ TAPA samples were commercial products sold under the trademark Primene by Rohm and Haas company. Chemicals used for the experimental studies were purchased from Aldrich Chemical Company. The antioxidants used for the experiments included N,N-dimethylcyclohexylamine, 2,6-di-t-butyl-4-methylphenol, N,N'-di-sec-butyl-p-phenylenediamine, and dinonyl diphenylamine. Organic acid co-dopants included dodecylbenzene sulfonic acid. Classes of nitrogen compounds employed included N,N-di-methylaniline, 4-dimethylaminopyridine, and 2,5-dimethylpyrrole. Co-dopants such as metals and t-butylhydroperoxide were also used.

II. Diesel Thermal Stability Tests: A modified Octel/Du Pont F21 test was used as follows. A 50 mL sample of fuel oil in a test tube is stored in a 300°F bath for 90 minutes (or 180 Min.). After removal from the bath it is allowed to cool to room temperature (about 2 hr.). The aged fuel is then filtered through 4.25 cm Whatman No 1 filter paper. The paper is then washed with heptane and the color of the filter paper is compared to a set of standards (1 = No color, 20 = dark brown). The data is given in Tables II and III. Thermal stability tests were also done by using pressurized differential scanning calorimetry.

III. Diesel Oxidation Stability Tests: A modified ASTM D2274 was used for oxidative stability tests as follows. A 350 mL sample of fuel is heated at 95°C for 16 hr. (or 40 hr.) while oxygen is bubbled through at the rate of 3 liters per hour. After aging, the sample is cooled to room temperature and filtered to obtain the filterable insoluble quantity. Adherent insolubles are then removed from the associated glassware with trisolvant (TAM). The TAM is then evaporated to obtain the adherent insolubles. The sum of filterable and adherent insolubles, expressed as milligrams per 100 mL, is reported as total insolubles. The data is given in Table V. In addition, oxidative stability was also measured by DSC experiments and by ASTM D942 test.

IV. Doping Studies: Various fuel samples were doped with precise amounts of additives (inhibitors, peroxides, acids, bases, etc.) The fuel stabilities were then measured as mentioned in the above experiments. In the case of hydroperoxide doping experiments, peroxide numbers were measured by the standard ASTM D3703 method. The results are calculated as milligrams per kilogram (ppm) of peroxide.

V. Solubility: Solubility experiments were carried out with salts of dodecylbenzenesulfonic acid with various basic nitrogen compounds such as 2,5-dimethylpyrrole, 4-dimethylaminopyridine, alkylated-phenylenediamines, and C₁₂ TAPA. Solubility of the pure salts was then studied in diesel. The Kauri-butanol value (KB Value, ASTM D1133) was used as a measure of solvent power of TAPA. The KB was calculated by standardization with toluene (assigned KB of 105) and heptane-toluene (assigned KB of 40) blend.

RESULTS AND DISCUSSION

Oxidative and thermal stability of diesel fuels was studied on fuel samples collected from major regions around the world; namely, North America, Latin America, and Asia. The results of the various stability tests as measured by color, sediments and gum formation show clearly that addition of TAPA, at few ppm levels, significantly improves the stability of diesels. Tables II and III show that the thermal stability of both low and high sulfur diesel fuels can be improved by TAPA doping at 8-40 ppm range. It is noteworthy that both sedimentation and color are improved by TAPA. The results of oxidative stability of diesel showing the similar TAPA benefits were shown earlier¹². Several commercial fuel stabilizers at the same dosage level show similar or worse performance. The data that TAPA are equal or better stabilizers is also seen in comparative experiments with several well-known fuel antioxidants. C₉ TAPA shows the best results for the low sulfur diesel when compared on equal weight basis with other stabilizers. Although diphenylamines improve the stability, hindered phenol was only slightly effective.

However, addition of phenylenediamine degraded both the filter pad rating and color. The fuel oil stability results using the C₁₂ TAPA in combination with a dispersant and/or a metal deactivator have shown that the performance over the TAPA alone is not significantly improved. The diesel data, in addition, shows the differences in activity of various TAPA additives. This data allows both dosage and structure-activity relationships establishment. The mechanism by which TAPA act as antioxidants is not completely understood, but an attempt is made here to form a general interpretation of their stabilization mechanisms. The mechanistic study here is done based on structure-activity relationship of TAPA coupled with results of stability tests under various conditions.

STRUCTURAL ATTRIBUTES OF TAPA

The feature of having a tertiary carbon attached to nitrogen is very beneficial because it imparts important characteristics⁸ to these amines. Table 1 lists some of the key TAPA properties of value in diesel stabilization. TAPA with branched alkyl groups have low viscosity and are liquids at room temperature whereas most long chain linear amines are solids⁹ at room temperature. Compared to linear alkyl primary amines the branched TAPA are readily soluble in fuel oils. In addition, these amines are also ashless and completely combustible. They are virtually insoluble in water and are not leached from fuels by contact with water during storage and handling. The fact that there are no α -hydrogens attached to nitrogen gives TAPA better oxidative stability because this weak C-H bond is most prone to oxidation. The lack of α -hydrogens also ensures that unstable imines are not formed which can deaminate in the presence of water. This makes TAPA oxidatively more stable than their corresponding linear amines. The oxidative stability of selected TAPA and their linear analogs were comparatively evaluated by DSC measurements¹⁰. In all cases the corresponding *n*-alkylamines decomposed before the TAPA indicating that the TAPA are oxidatively more stable than corresponding linear primary amines. Oxidation is the most common form of degradation of fuels. Hindered phenols and amines are commonly used as oxidation inhibitors and work by interrupting radical chain reactions. The chain carrying peroxy radical is scavenged by the phenol or amine by hydrogen atom donation. The resulting radicals are resonance stabilized and are eventually destroyed by reaction with another peroxy radical. Hindered amines, such as TAPA, can also react with free radicals to form stable intermediates that do not readily take part in chain reactions. Although they are not as resonance stabilized, they can regenerate by scavenging another hydrogen radical. A common test used to evaluate the antioxidant properties of additives involves heating base fluid in the presence of 0.5 - 1.0 % inhibitor at 120°C in an oxygen pressurized bomb and measuring the oxygen pressure drop as a function of time. We found¹¹ both C₁₂ and C₁₈ TAPA inhibited the oxidation of petroleum fluids. These TAPA proved similar to some commercially used phenolic and aminic antioxidants.

ACID SCAVENGING

Hazelett has shown¹³ the correlation of carboxylic and sulfonic acids in increasing deposit formation. The reaction of certain acidic compounds, such as naphthalene sulfonic acid, with nitrogen compounds, such as indoles, quinolines, and carbazoles, appears to be one of the mechanisms for fuel insolubles formation. Dodecylbenzenesulfonic acid promotes⁴ sediment formation and also may become incorporated into the sediment. Amine based stabilizers can react with acidic species preferentially. For weak acids, the amines exhibit more than 1:1 action and certain amines exert favorable behavior only if they are strong organic bases. TAPA are strong bases¹⁴ and can readily react with acidic species, sacrificing themselves to form salts that are miscible in these liquids and thus do not precipitate. In salt formation, two TAPA attributes are very important. First, the high basicity exhibited by these amines, in non-polar media such as fuels, allows very efficient and complete scavenging of both strong and weak acids. Furthermore, the branched and hindered carbon chain of TAPA helps envelop the salt thereby better solvating it. We have recently done¹⁴ pK_a measurements on these amines using both reaction calorimetry and quantum chemical estimates and find that TAPA are stronger bases than corresponding linear primary amines in non-polar solvents.

REDUCTION OF HYDROPEROXIDES

Sediments that form in diesel fuels are often the direct result of autoxidation reactions involving hydroperoxides³. Thus, increasing peroxide concentration is often an indicator of the instability. The peroxides can stimulate insolubles by two processes. One is by converting thiols and aldehydes to sulfonic and carboxylic acids which act as acid catalysts and sediment promoters. The second is by a free-radical mechanism, possibly by oligomerizing olefins and by addition of the thyl radical to olefins. Induced decomposition of hydroperoxides can be catalyzed by metals, acids, and amines. The catalytic efficiency of the amines generally correlates with their ionization potentials. This correlation supports the mechanistic interpretation that a charge

transfer complex between the amine and the peroxide weakens the O-O bond. Quenching by amines is also subject to steric effects. Tertiary amines have been well-studied as hydroperoxide scavengers, but not much is known about TAPAs. However, oxidation of mercaptans in sour fuels to disulfides by organic hydroperoxides has been shown¹⁵ to be catalyzed efficiently by C₁₂ TAPA. We studied the effect of added hydroperoxide to the fuel by measuring both the oxidative stability and concentration of peroxides (See Table IV). As anticipated, addition of hydroperoxide greatly destabilizes the fuel by showing much higher amounts of gum and sediments than in the undoped sample. Also as expected, addition of 2, 5-dimethylpyrrole further increases the sediment formation. However, addition of TAPA greatly increases stability as measured by the reduction in sediment and also reduces the peroxide concentration. The effect of TAPA on reducing sediments is better than that shown by both the secondary and tertiary amines.

SOLUBILIZATION AND DISPERSANCY

For a good stabilizer, it is important not only to mitigate the oxidative process, but also to help resolve problems caused by them. Not only are the TAPAs soluble in base oil but many salts of oil insoluble organic and inorganic acids of these TAPA are completely miscible in base oil. We have studied¹⁰ the solubility of several inorganic and organic salts of TAPA in kerosene and white mineral oil. For example the TAPA salts of EDTA, trichloroacetic acid, molybdic acid, tungstic acid, and sulfuric acid are readily soluble (>20%) in mineral oil compared to their free acid. TAPA can act by forming fuel soluble salts with acidic by-products of oxidation. Furthermore, their complexation with metals and other species can allow suspension of gums and particles. By keeping the sediment particles from agglomerating they can be kept small enough to be dispersed through the fuel filters. Molecular modeling shows that the resulting complexes can effectively shield the metal atoms thereby reducing their ability to catalyze degradative reactions. The role of TAPA in minimizing gums and sediment formation by "solvating ability" of the branched alkyl chains of TAPA is also likely. The high Kauri Butanol values measured are indicative of that. For the C₁₈ TAPA the KB value of more than 119 compares well with that of only 30-35 seen for the diesel. The decreased sediment seen, in both the thermal and oxidative tests, is most likely in part due to better solvent properties¹⁶. To confirm this theory, we prepared salts of model acidic compounds (Dodecylbenzenesulfonic acid) with various amines. The pure salts were then tried to dissolve in diesel fuel at various levels. The results can be seen in Table V. It was noted that acid salts of TAPA were not solids, unlike other amine salts, and could be readily dissolved in the diesel. Furthermore, these salts had much lighter color than the salts prepared from phenylenediamines.

CONCLUSIONS

We have shown that deterioration is delayed, color degradation is inhibited and sludge formation is reduced by addition of TAPA to the diesel fuels. The tertiary alkyl primary amines are highly effective stabilizers for the prevention of sludge and color formation under both thermal and oxidative stress. Their performance is equal or better than many other commonly used fuel stabilizers. They inhibit the reactions responsible for sludge formation and also disperse the gum and sediment from depositing. The additive concentration and structure effect suggest that the stabilization properties of TAPA result from factors such as acid scavenging, hydroperoxide decomposition, dispersing of gums and particulates, or any combination of these factors. The several established fuel degradation mechanisms pathways can be prevented or resolved by the use of these amines.

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Table I. Tertiary Alkyl Primary Amine Properties

Property	TAPA C ₉	TAPA C ₁₂	TAPA C ₁₈
Chemical name	t-nonylamines	t-dodecylamines	t-octadecylamines
Molecular Weight	143 (average)	185 (average)	269 (average)
Boiling Range (°C)	170-180	220-240	265-305
Pour point	-85°C/ -185°F	<-59°C/-74°F	<-40°C/-40°F
Base Strength (pKa)	11	11	11
Water solubility at 25°C	0.53%	1000 ppm maximum	900 ppm max
K _p (Water/Heptane)	0.00772	0.0036	0.0031
Surface tension at 20°C (dynes/cm ² , ASTM D-1331)	27	30	31
Interfacial Tension with water (dynes/cm ² , ASTM D 971)	1.5	2	8
Kauri-Butanol Value (ASTM-1133)	20	35	>119
Thermal Stability by DSC	>500°C	>500°C	>500°C

Table II. Thermal Stability Test Results Using Du Pont F-21 @ 150°C/90 Min.

Additives (ppm)	Diesel #1		Diesel #2		Diesel #3		Diesel #4	
	Filter Pad Rating	ASTM Color						
Sulfur Content	0.24%		0.38%		0.56%		0.72%	
None	11	2.5	16	5	16	6	18	5
TAPA C ₁₂ (8.5)	3	2	4	3.5	3	4	2	3
TAPA C ₁₂ (17)	2	2	2	3.5	4	3.5	2	2.5
TAPA C ₁₂ (35)	2	2	3	3	4	3	3	2.5
Commercial AO #1 (8.5)	5	2	2	3	6	4	4	3
Commercial AO #1 (17)	2	2	3	3.5	4	4	4	2.5
Commercial AO #1 (35)	2	2	2	3.5	2	3.5	5	2.5
Commercial AO #2 (8.5)	3	2	11	2	10	3.5	8	2
Commercial AO #2 (17)	3	2	10	2	7	3	8	2
Commercial AO #2 (35)	2	2	7	2	6	2.5	6	2

Table III. Thermal Stability Test Results of Using Du Pont F-21 test @ 150°C /180 Min.

Additives (ppm)	Diesel #5	
	Filter Pad Rating	ASTM Color
Sulfur Content	0.04%	
None	13	1.5
TAPA C ₁₂ (20)	9	1.5
TAPA C ₉ (20)	10	1.5
2,6-di-t-butyl-4-methylphenol (20)	11	1.5
2,6-di-t-butyl-4-methylphenol (40)	12	2
N,N'-di-sec-butyl-p-phenylenediamine (20)	14	2.5
N,N'-di-sec-butyl-p-phenylenediamine (40)	14	2.5
Dinonyl diphenylamine (20)	9	2.5

Table IV Comparative Oxidation Stability (ASTM D2274 @ 40 hr) with Added Peroxide and Stabilizers

Diesel + additives *	Total Insolubles (mg/100 ml)	Peroxide, ppm (before 2274)	Peroxide, ppm (after 2274)
Blank	0.1	0.1	4.5
+ t-BHP	1	99.8	25.6
Dimethylpyrrole + t-BHP	57.6	58.6	2.3
Dimethylcyclohexylamine + t-BHP	1.5	>118	2
Dinonyl diphenylamine + t-BHP	0.6	92.8	5.3
N,N'-di-sec-butyl-p-phenylenediamine + t-BHP	5.4	97.7	8.7
TAPA C ₉ + t-BHP	0	97.9	10.9
TAPA C ₁₂ + t-BHP	0.1	99.1	14
TAPA C ₁₈ + t-BHP	0	90.8	19

* For the doping experiments, following amounts were used: t-butylhydroperoxide at 100 ppm peroxide and stabilizer at 135 ppm Nitrogen concentration.

Table V. Solubility of Dodecylbenzene Sulfonic Acid Salts of Aminic Bases* in Diesel

Aminic Bases	0.1% in diesel	0.2% in diesel	0.5% in diesel	0.7% in diesel	Comments
TAPA C ₁₂	Soluble	Soluble	Soluble	Soluble	The salt is a light colored gum
4-(dimethylamino)-pyridine (solid)	Soluble	Soluble	Soluble	Slightly soluble	The salt was made using diesel as a solvent, light colored paste, and foamy when mixed with diesel
2,5-Dimethylpyrrole	Not soluble	Not soluble	Not soluble	Not soluble	The salt was made using diesel as a solvent, dark colored gum
N,N'-di-sec-butyl-phenylenediamine	Not soluble	Not soluble	Not soluble	Not soluble	The salt was made using diesel, dark colored gum

* Salt was prepared by reacting Dodecylbenzene sulfonic acid and aminic bases at 1:1 equivalent ratio