

# TERTIARY ALKYL PRIMARY AMINES AS STABILIZERS FOR MIDDLE DISTILLATE FUELS

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## ABSTRACT

Degradation of middle distillate fuels under both the prolonged storage and high-temperature thermal stress is of concern. There is a continued challenge in developing stabilizers that are increasingly cost-effective, do not degrade the performance of fuel, and are environmentally acceptable. We are interested in developing branched tertiary alkyl primary amines (TAPA) as multi-functional fuel additives. They are ashless, combustible, and nonextractable stabilizers. The results of stability experiments for thermal and oxidative degradation of various middle distillate fuels (diesel, jet fuel, fuel oil) are presented. The TAPA, individually and in combination with other additives, are evaluated in these stability tests. An attempt is made to form a general interpretation of stabilization mechanisms of TAPA as radical chain breakers, peroxide decomposers, metal deactivators, solubilizers, dispersants, and as acid scavengers.

## INTRODUCTION

The useful life of fuel is a function of its quality and of storage conditions. Depending on the crude source and amount of cracked fraction, middle distillate fuels can contain very different amounts of gum and color precursors, waxes, aromatics, and other products. Estimated useful life<sup>1</sup> of good quality middle distillate fuels, under normal storage conditions, varies from about 1 year for Diesel and Heating fuel to 3-4 years for Jet fuels. However, fuels are often stored for much longer periods because of logistical and economic necessities. This is particularly so for military use where it is necessary that the fuel quality remains fit for use throughout the storage period. Both the low-temperature storage and high-temperature thermal degradation, are of concern. There may be a relationship between the chemistry of deposit formation during normal long term storage and the deposits obtained by thermal stressing of jet fuel.

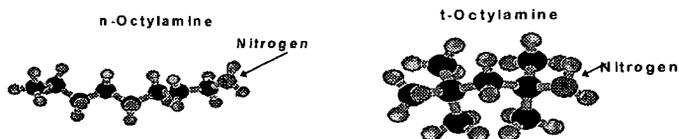
Fuels containing higher amounts of olefins, certain nitrogen and sulfur compounds, organic acids, or dissolved metals are likely to degrade more and faster. Sediments and gums which result from the oxidation reactions act to block filters and deposit on surfaces. The progressive lowering of sulfur levels has greatly reduced the instability of diesel. On the other hand, potential new problems resulting from increased processing and the resultant removal of natural antioxidants has occurred. Additionally, to meet increasing demands for fuels, refiners have turned to blending significant proportions of cracked stock as middle distillate fuel extenders. The cracking process produces components of lower stability than straight-run distillates.

Hydrotreating is generally considered the most effective means of improving the stability. However, often the cost of stability improvement by additives doping can be less than the hydrotreatment costs. Demand for additives in these markets is projected (The Freedonia Group estimate) to increase nearly 15% a year to \$350 million in 1998. The stability enhancing additives for middle distillate fuels include hindered phenols (jet fuels), phenylenediamines, tertiary amines, metal deactivators and dispersants. Tertiary amines are generally considered<sup>2</sup> better than secondary or primary amines as fuel antioxidants.

Phenylenediamine type antioxidants are more effective than hindered phenols in neutralizing peroxides. Research<sup>3</sup> on peroxide formation in several diesel fuels found that low sulfur and aromatics content fuels (Swedish fuels) are likely to form more peroxides upon aging. 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.<sup>3b</sup> Phenylenediamines have been shown to participate in side reactions forming sediments<sup>3a</sup> and increasing color body formation.<sup>3c</sup>

Primary amines have not received much attention as fuel stabilizers because they are not considered as good radical/peroxide quenchers as secondary or tertiary amines. This is true for typical straight-chain fatty amines. However, we are mainly interested in a special class of primary amines that possess branched alkyl chains with the primary amino group attached to a tertiary carbon. We will refer to these as tertiary alkyl primary amines (TAPA).<sup>4</sup> This feature of having a tertiary carbon attached to nitrogen is very beneficial because it imparts important

characteristics<sup>5</sup> to these amines. The structural differences between fatty and TAPA amines are illustrated in the following figure.



Branched tertiary alkyl primary amines possess<sup>6</sup> excellent oil solubility, thermal and oxidative stability, strong basicity, and fluidity over a wide temperature range. These properties make them well suited for enhancing the performance of petroleum fluids<sup>7</sup> as well as lubricants.<sup>8</sup> The fact that there are no  $\alpha$ -hydrogens attached to nitrogen gives TAPA better oxidative stability because this weak C-H bond is most prone to oxidation. The lack of  $\alpha$ -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 fact that TAPA can be used as fuel stabilizers, and are better than normal primary amines, was first shown in 1960.<sup>9</sup> We will describe the work carried out at Rohm and Haas research laboratories with TAPA, individually and in combination with other additives, for their ability to stabilize middle distillates.

## EXPERIMENTAL

Fresh test fuels 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 purifications. All the C<sub>8</sub>, C<sub>12</sub>, and C<sub>18</sub> TAPA samples were commercial products sold under the trademark Primene by Rohm and Haas company. The details of the stability test methods are given below.

**I. Furnace Oil Stability Test:** Fuel samples of 500 mL were stored in 600 mL beakers covered with watch glasses in oven at 40°C. At arbitrary intervals, optical density measurements were made on samples before and after filtering a small portion of vigorously shaken sample through a CORNING 30 F fritted glass crucible. The unused portion was immediately returned to the oven for further aging. The failure time was determined by three methods: 1) the number of days to a stated level of optical density difference ( $\Delta$  OD) of 0.12 between unfiltered portions, 2) days to reach an OD value of 1.00 for the unfiltered sample, and 3) days to reach a residue level of 2.0 mg/100 mL as determined by filtration. The data is given in Table I.

**II. Fuel Oil No. 2 Stability Test:** A 50 mL sample of fuel oil in a test tube is stored in a 300°C bath for 90 minutes. 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). A color of 7 or less is considered acceptable. The data is given in Table II.

**III. Modified ASTM 2274 Diesel Oxidation Stability:** 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 trisolvent (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 III.

**IV. Thermal Oxidation Stability of Jet Fuels (JFTOT):** 600 mL of test fuel is pumped at a rate of 3 mL/min through an aluminum heater tube (JFTOT apparatus) at 260°C (or 325°C) for 150 minutes, and passed through a 17  $\mu$ m SS filter. The essential data derived is the amount of deposits on the heater tube, and the rate of plugging of the filter (pressure drop). The deposits on the heater tube are rated by the ASTM Color Standard. The data is given in Table IV.

## RESULTS AND DISCUSSION

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 fuel oils and diesel. Table I shows that the stability of catalytically cracked furnace oil can be improved by C<sub>12</sub> TAPA doping at 30 ppm. Several commercial fuel stabilizers at the same dosage level show similar or worse performance. Similar behavior is noted for the No. 2 fuel oil stability. The data

that TAPA are equal or better stabilizers is also seen in comparative experiments with two commercial additives. The fuel oil stability results using the C<sub>12</sub> TAPA in combination with a dispersant and/or a metal deactivator show that the performance over the TAPA alone is not significantly improved. Oxidative stability of diesel fuel was studied on fuel samples collected from three major regions around the world; namely, North America, Latin America, and Asia. Once again, improvement in the oxidative stability is obvious with the addition of 30 ppm of TAPA. The diesel data, in addition, shows the differences in activity of various TAPA additives. This data allows both dosage and structure-activity relationships establishment. Furthermore, JFTOT tests with TAPA show improvement in thermal stability benefit. Particularly noteworthy is the effect seen at 325 °C heat exposure. This is significantly higher exposure than the traditional 260 °C tests. This result is not only supportive of TAPA benefit, but important in light of the current need to develop aircraft fuels which can operate under supercritical conditions.

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 sediment and gum formation mechanisms have been studied in great details<sup>2-10</sup> and can be summarized<sup>3</sup> 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. 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 additive concentration and structure effect suggest that the stabilization properties of TAPA result from factors such as radical scavenging, acid scavenging, hydroperoxide decomposition, metal deactivation, dispersing of gums and particulates, or any combination of these factors.

#### **CHAIN BREAKING MECHANISMS**

Hindered phenols and aromatic amines are considered radical chain breakers. 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 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.

#### **REDUCTION OF PEROXIDES AND HYDROPEROXIDES**

Amines in general, and tertiary amines in particular, are well known peroxide decomposers. The catalytic efficiency of the amines generally correlate 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.

#### **METAL DEACTIVATORS**

It is anticipated that middle distillates will have a higher metal content<sup>11</sup> than gasoline, and the content increases with increasing metal contents of the crude. Complexes of Fe, Mn, Co, and Ni, when solubilized as fuel soluble salts, are all known to be oxidation catalysts and are present in most middle distillate fuels in trace amounts. These metals will promote oxidation of the fuel with subsequent gum formation and deposit build-up. The MDA is believed to form a caged complex with dissolved metal salts (especially copper) that is generally less active as an oxidation catalyst than the free metal itself. TAPA can also effectively chelate these metal atoms. Molecular modeling shows that the resulting complexes can effectively shield the metal atoms thereby reducing their ability to catalyze degradative reactions. The TAPA also migrate to new surfaces, further inhibiting the formation of soluble metal salts. Their filming action can also lead to protection of metal surfaces and thus inhibiting metal ions solubilization.

#### **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. TAPA act by forming fuel soluble salts with acidic by-products of oxidation. Furthermore, their complexation with metals and other species allows suspension of gums and particles. The role of TAPA in minimizing gums and sediment formation by "solvating ability" of the branched alkyl chains of TAPA is also likely. By keeping the sediment particles from agglomerating they can be kept small enough to be dispersed through the fuel filters. Despite their dispersant action they are unlike many additives that cause emulsions when fuels containing them mix with water. In fact, they also act as demulsifiers and provide another benefit to the fuel storage.

## ACID SCAVENGERS

Hazelett has shown<sup>12</sup> 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 promotes sediment formation and also may get incorporated into the sediment. Tertiary amines were shown<sup>12</sup> to be effective in reducing deposits in fuel blends containing acids. 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 bases<sup>13</sup> and can readily react with acidic species, sacrificing themselves to form salts that are miscible in these liquids and thus do not precipitate.

## CONCLUSIONS

We have shown that Fuel deterioration is delayed, color degradation is inhibited and sludge formation is reduced by addition of TAPA to the middle distillate fuels. The tertiary alkyl primary amines are highly effective stabilizers for the prevention of sludge formation in fuel oils and diesel and their effectiveness depends on the structure of the amine. They inhibit the reactions responsible for sludge formation and also disperse the gum and sediment from depositing. They also improve the thermal stability of jet fuels. 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. Additionally, they do contribute beneficially to other fuel properties. Corrosion inhibition is another benefit that can be obtained by the use of TAPA. Water contained within fuel, or permeating from external sources, combines with air to attack iron to form rust. This can be prevented by protecting metallic surfaces with an additive film by using TAPA or their salts. The polar portion of the molecule adheres to the metal surface and forms the protective film.

## ACKNOWLEDGMENTS

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**TABLES**

**Table I. Fuel Oil Stability Test (Catalytically Cracked Furnace Oil)**

Additive	Dosage (ppm)	Days to failure		
		Δ OD	OD = 1.00	2 mg/100 mL
None	----	38	71	60
C <sub>12</sub> TAPA	30	94	120	68
Commercial AO #A	30	35	105	85
Commercial AO #B	30	36	88	58
Commercial AO #C	30	54	107	63
Commercial AO #D	30	64	104	75

**Table II. Accelerated Storage Stability Tests (No. 2 Fuel Oil)**

Additive	Dosage (ppm)	Louisiana Sample		Mid-West Sample	
		Filter Pad Rating	ASTM Color	Filter Pad Rating	ASTM Color
None	---	11	205	16	6
C <sub>12</sub> TAPA	7.5	3	2	3	4
"	15	2	2	4	3.5
Commercial AO #1	7.5	5	2	6	4
"	15	2	2	4	4
Commercial AO #2	7.5	3	2	10	3.5
C <sub>12</sub> TAPA+MDA	7.5+1.5	3	2	4	4
C <sub>12</sub> TAPA+Dispersant	7.5+7.5	3	2	3	4
C <sub>12</sub> TAPA+Dispersant+MDA	7.5+7.5+1.5	7	2	7	3.5

**Table III. Oxidative stability Results Using ASTM 2274 Test Method(Diesel)**

Additives	Dosage (ppm)	Insolubles mg/100 mL			
		Gulf Coast Sample A	LAR Sample	Asian Sample	Gulf Coast Sample B
None	---	1.1	0.5	2.2	2.3
C <sub>12</sub> TAPA	100	<0.1	0.3	0.3	---
C <sub>18</sub> TAPA	100	0.1	0.6	---	---
C <sub>8</sub> TAPA	15	---	---	---	<0.1
TAPA #A	15	---	---	---	0.9
C <sub>12</sub> TAPA	15	---	---	---	1.2
TAPA #B	15	---	---	---	<0.1
C <sub>18</sub> TAPA	15	---	---	---	1.4
TAPA #C	15	---	---	---	1.9

**Table IV. Thermal Oxidation Stability Using (JFTOT) ASTM -D 3241(Jet Fuel)**

Additives	Dosage (%)	Preheater Tube Deposit	Pressure Drop	Comments
None	---	3	30	@ 260°C
C <sub>12</sub> TAPA	1	2	4	@ 260°C
C <sub>18</sub> TAPA	1	2	2	@ 260°C
None	----	1	6	@ 260°C
C <sub>18</sub> TAPA	0.1	1	<1	@ 260°C
None	----	4	2	@ 325°C
C <sub>18</sub> TAPA	0.1	<4	<1	@325°C