

MECHANISMS OF NITROGEN HETEROCYCLE INFLUENCE ON TURBINE FUEL STABILITY*

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Lewis bases were extracted from a Utah COED syncrude via ligand exchange. Addition of this extract to Jet A at levels as low as 5 ppm N produced deterioration of stability in both JFTOT and accelerated storage tests (7 days at 394°K with 13:1 air to fuel ratio). Comparable effects on Jet A stability were obtained by addition of pyridine and quinoline, while pyrrole and indole were less detrimental at the same concentration level. These four compounds represent the compound classes predominant in the extract.

The weight of deposit produced in accelerated storage tests was found to be proportional to the concentration of added nitrogen compound. Over the narrow temperature range accessible with the experimental method, Arrhenius plots obtained by assuming specific rate to be proportional to the weight of material deposited in seven days exhibit greater slopes in the presence of those nitrogen compounds producing the greater deposition rates. Despite variation in appearance the elemental composition and spectral characteristics of the deposits are unaffected by addition of the nitrogen compounds. The linearity of the Arrhenius plots and of a plot of Arrhenius slope versus intercept for all the compounds suggests a constancy of mechanism over the range of temperature and heterocycles studied.

A suite of twenty-three nitrogen heterocycles representing a wide range of basicities and electronic and steric environments at the nitrogen atom was selected. Added to Jet A at the level of 5 ppm N, these compounds increased deposition rates in proportion to their basicities within a given compound class (pyridines, pyrroles, indoles, and quinolines). No general correlation with basicity between compound classes was found. Compounds in which the nitrogen atom is sterically hindered were found to be much less detrimental than expected on the basis of basicity. Analogous experiments were performed using a Diesel fuel. Although higher absolute deposition rates were obtained, the nitrogen compound effects were entirely parallel. Silica gel treatment greatly increased stability of the fuel, even in the presence of added heterocycles.

A model system composed of tetralin in dodecane was shown to exhibit behavior very similar to that observed for Jet A and Diesel fuels. Although the absolute deposition rate was significantly lower, nitrogen heterocycles produced increases in deposit formation in approximate proportion to their basicities. However, the rate of decrease in tetralin concentration was not significantly altered. Decomposition of tetralin hydroperoxide, the primary auto-oxidation product, markedly increased upon addition of quinoline. While tetralin hydroperoxide in dodecane produced deposits more rapidly than did tetralin itself, much greater deposition occurred when both tetralin hydroperoxide and tetralone (one of the decomposition products of the hydroperoxide) were

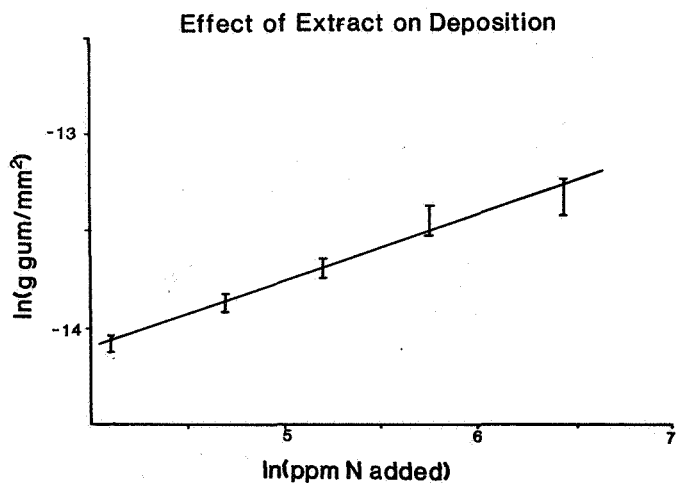
*NASA Grant NSG-3122.

present. These observations and that of base catalysis by the nitrogen heterocycles is consistent with the involvement of condensation reactions (perhaps between the hydroperoxide and the ketone) in the rate-controlling step of deposit formation in the model system. Multiple-internal-reflectance infrared spectra demonstrate the presence of carbonyl and hydroxyl groups in both model system and Jet A deposits.

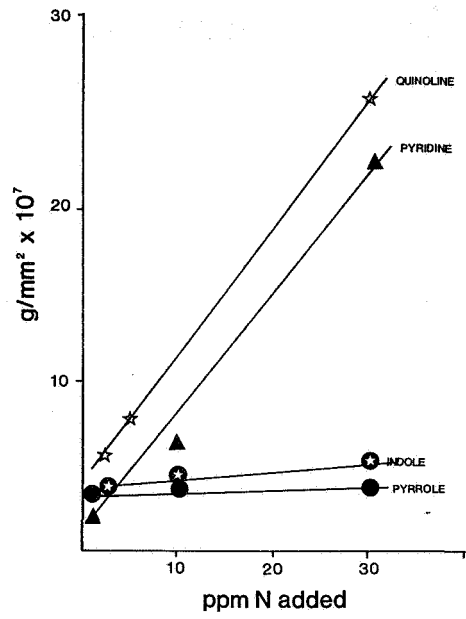
Elemental analyses, spectra, and chromatographic results all indicated remarkable similarities between the model system deposits and those obtained from Jet A. Parallelism in the mechanism of deposition is therefore inferred.

Deposit (168 hr, 120°C) from Spiked Jet A

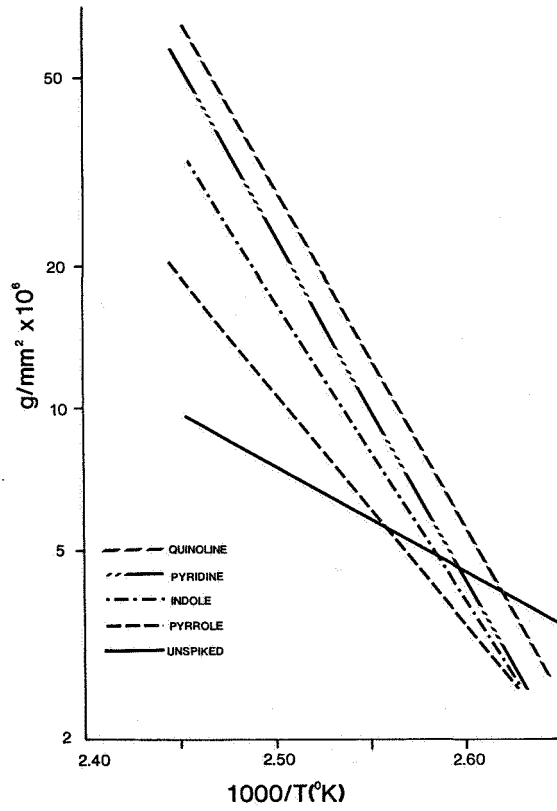
Spiking Compound	(g deposit/mm) x 10 ⁷	PKa
Control (no spike)	3.4 ± .3	--
Pyrrole	3.5 ± .5	-3.8
N-Methylpyrrole	8.7 ± .6	-2.90
2-Pyrrolidone	4.2 ± .8	--
1,2,5-Trimethylpyrrole	3.7 ± .3	- .24
Indole	3.9 ± .3	-2.4
N-Methylindole	3.6 ± .3	-1.80
2-Methylindole	5.9 ± .3	- .10
3-Methylindole	2.3 ± .5	-3.35
Indoline	6.7 ± .2	--
Carbazole	2.6 ± .3	--
N-Ethylcarbazole	4.4 ± .6	--
Pyridine	3.6 ± .3	5.22
2-Acetylpyridine	3.5 ± .5	--
2-Methylpyridine	7.9 ± .8	5.94
4-Methylpyridine	8.8 ± .5	6.03
2-Ethylpyridine	5.9 ± .3	5.93
2,6-Dimethylpyridine	10.0 ± 1.4	6.64
2,4,6-Trimethylpyridine	4.7 ± .2	7.43
Quinoline	7.7 ± .0	4.85
2,4-Dimethylquinoline	8.2 ± .7	5.12
7,8-Benzoquinoline	2.8 ± .5	4.3
4-Hydroxy-2-methylquinoline	9.1 ± .4	--
8-Hydroxyquinoline	8.1 ± .2	4.91



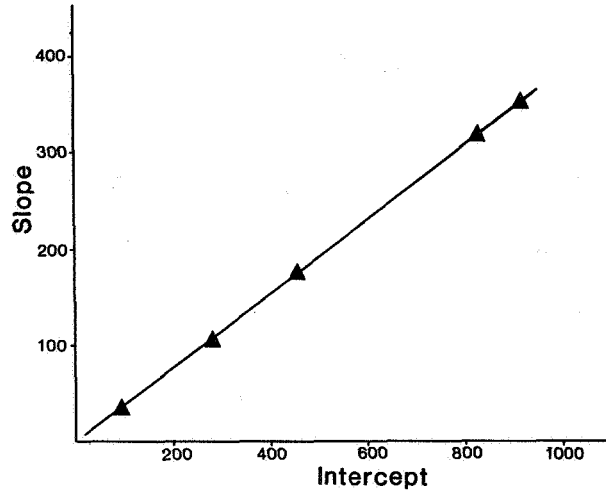
Effect of Added Nitrogen Concentration on Deposition Rate



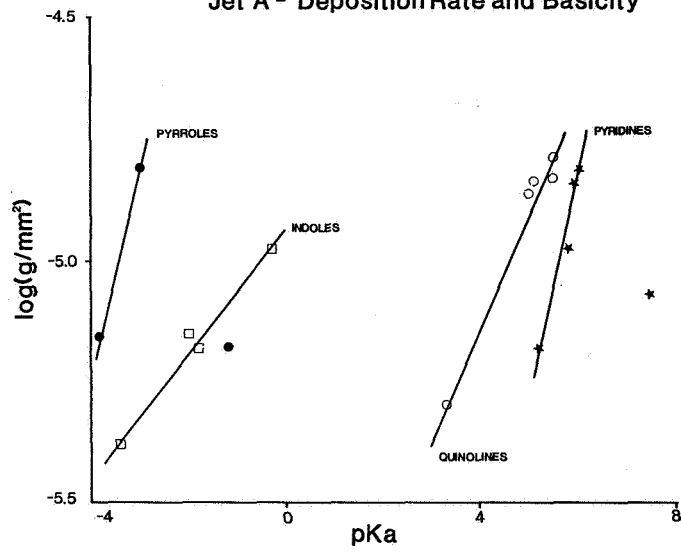
Temperature Dependence of Deposit Formation



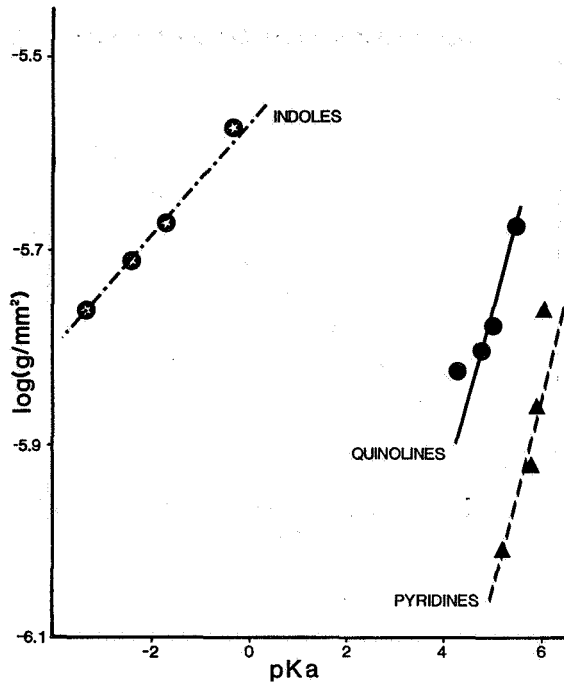
Arrhenius Slope/Intercept Relationship



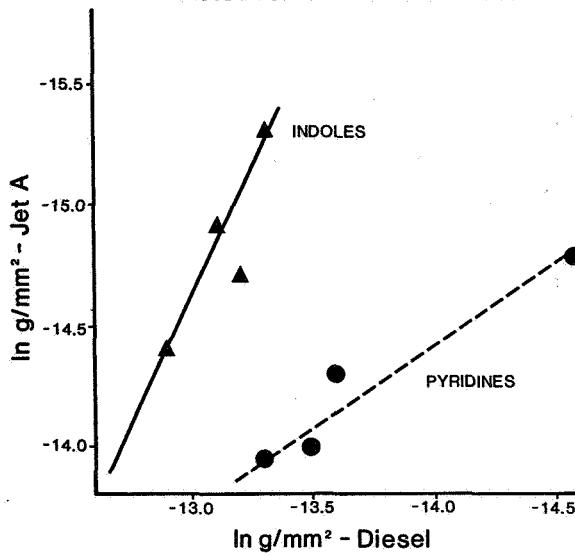
Jet A - Deposition Rate and Basicity



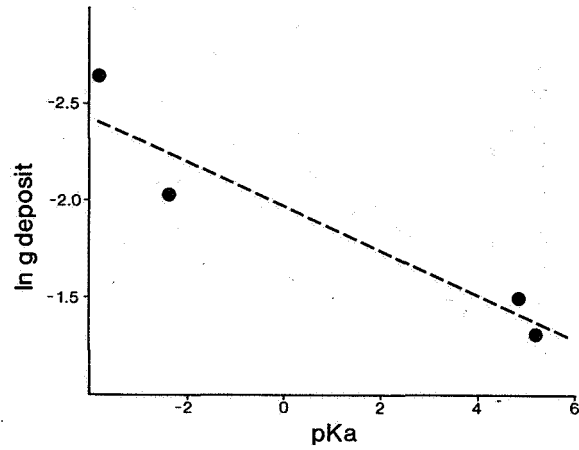
Diesel - Deposition Rate and Basicity



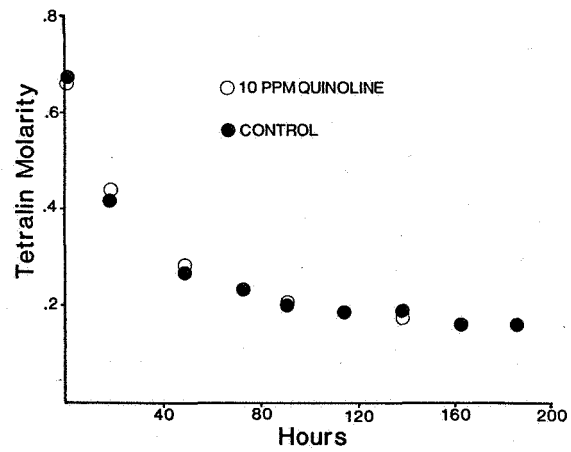
Comparison of Nitrogen Compound Effects in Jet A and Diesel Fuels



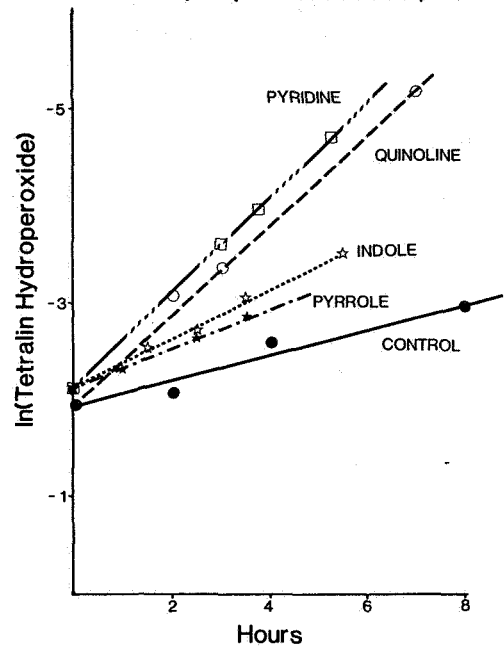
Effect of Nitrogen Heterocycles on Deposit Formation in the Model System



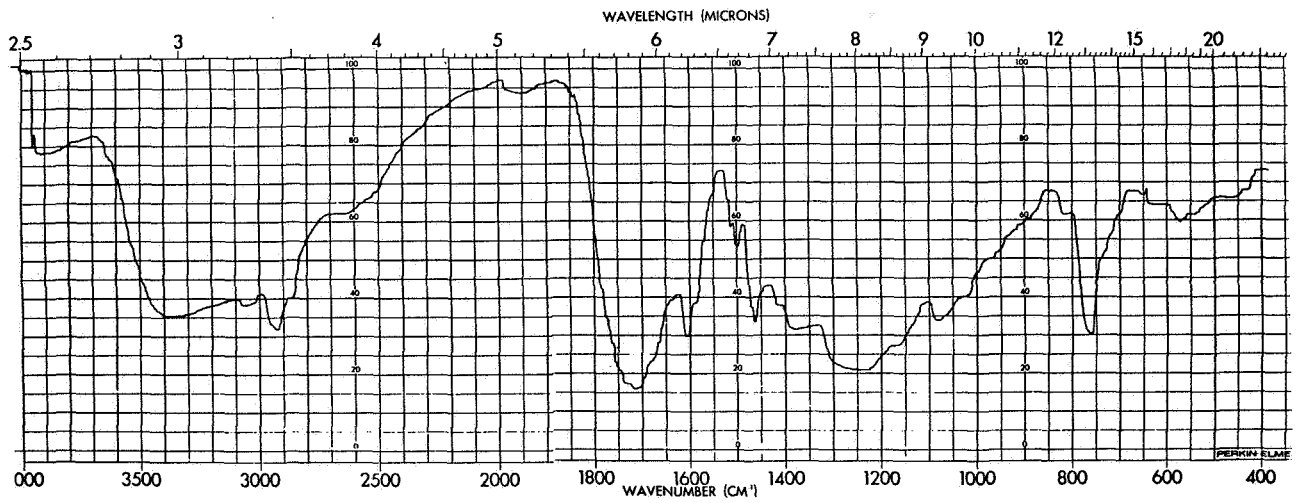
Effect of Quinoline on Tetralin Auto-oxidation



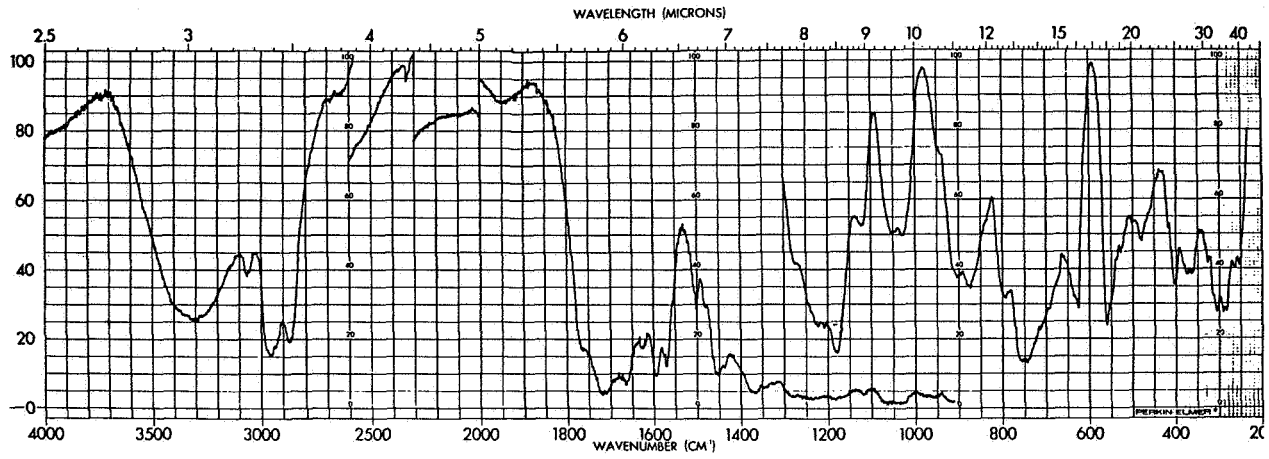
Effect of Nitrogen Heterocycles on
Tetralin Hydroperoxide Decomposition



TRANSMISSION SPECTRUM OF MODEL SYSTEM STORAGE DEPOSIT



MULTIPLE INTERNAL REFLECTANCE SPECTRUM OF MODEL SYSTEM STORAGE DEPOSIT



MULTIPLE INTERNAL REFLECTANCE SPECTRUM OF JET A STORAGE DEPOSIT

