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STUDIES OF THE MECHANISMS OF TURBINE FUEL INSTABILITY

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SUMMARY

The mechanisms of storage and thermal instability of turbine fuels were investigated through determination of the effects on stability of:

1. Addition of a Lewis base extract from a coal-derived liquid to Jet A.
2. Addition of individual nitrogen heterocycles to Jet A and to a Diesel fuel.
3. Removal of polar constituents of Diesel and then readdition of various fractions of the extracted material to the fuel.
4. Addition of individual organic sulfur compounds, of copper metal, and of copper salts to Jet A.

Lewis bases extracted from the coal liquid decreased Jet A stability to an extent comparable to that obtained by addition of individual nitrogen heterocycles at the same nitrogen concentration. The influence on stability of individual nitrogen heterocycles is dependent upon basicity, structural type, and steric effects. Considerable variation in effectiveness toward deposit-promotion occurs with sulfur compounds: thiols and dibenzothiophene increase deposit formation while sulfides and disulfides function as inhibitors. Both copper metal and soluble copper salts accelerate deposition in very similar fashion. Deposit is not formed on the metal surface.

A model "fuel" consisting of 1/10 (V/V) tetralin/dodecane was shown to exhibit stability behavior similar to the real fuels. A high-performance liquid chromatography (HPLC) method for analysis of deposit precursors in the model fuel was developed. Reactions leading to deposit formation in the model were investigated. Similarities in model fuel and Jet A deposits were demonstrated by elemental analyses, secondary-ion mass spectrometry, and multiple-internal-reflectance infrared spectrophotometry. The use of HPLC to monitor fuel degradation and correlation of results with stability tests were explored.

Nitrogen heterocycles catalyze deposit formation in the model system (tetralin/dodecane). This effect is attributed to base catalysis of both the decomposition of tetralin hydroperoxide and condensation reactions of the hydroperoxide and tetralone. Tetralol inhibits deposit formation. The presence of hydroxyl, carbonyl, and peroxy functional groups in both model and Jet A deposits was demonstrated. Secondary-ion mass spectra of the model deposit and Jet A storage and thermal deposits are compared.

INTRODUCTION

The mechanisms of storage and thermal instability of turbine fuels were investigated under NASA grant NSG 3122. The principal objective of the study was identification of those compositional characteristics of the fuels responsible for instability. Special attention was devoted to those composition parameters expected to differ greatly in fuels derived from petroleum and alternate sources.

Storage stability, the resistance to formation of non-volatile gums and solids during storage of hydrocarbon fuels, has been the subject of many studies. Much of the terminology and methodology developed in investigations of gasoline storage stability during the nineteen-thirties remains in use today. Autoxidation of hydrocarbons forming organic peroxides was identified as the initial reaction leading to formation of gums (Ref. 1-13). Yule and Wilson (Ref. 14) showed that the amount of gum formed on evaporation of a gasoline sample is proportional to the concentration of peroxides in the fuel. The reactions of these intermediate peroxides leading to gum were not elucidated. Most subsequent investigations sought to identify those components of the gasoline susceptible to autoxidation. Flood (Ref. 6) and Martin, et.al. (Ref. 7) identified olefins and diolefins as especially deleterious. Egloff, et.al. (Ref.8) found synergic olefin-diolefin interactions. The extent of gum formation was found dependent upon peroxide number but independent of aldehyde and acid (presumed peroxide decomposition products) concentrations (Ref. 7,8,9).

Nitrogen and sulfur compounds decrease stability and these elements become concentrated in the deposits (Ref. 15,16). Mapstone (Ref. 17) reported destabilization of a shale-oil gasoline by pyrroles but stabilization by pyridines. The presence of various metal surfaces and metal salts has been found to increase deposition rates (Ref. 18,19,20). Copper was reported most active while cobalt, chromium, iron, and lead all decrease stability.

Distillate fuel storage stability has been studied to a lesser extent. Clinkenbeard (Ref. 21) attributed instability to reactions of hydrocarbon autoxidation products with sulfur, oxygen, and nitrogen compounds. Elmquist (Ref. 22) stated that stability is affected by easily-oxidized aromatic thiols, reactive hydrocarbons, and oxygen. Thompson, et.al. (Ref. 23) found considerable variation among various organic sulfur compounds in effect on stability. Pyrroles were found more deleterious than pyridines (Ref. 24,25). Metal storage containers were shown to accelerate deposit formation in Diesel fuels (Ref. 26).

Johnson, et.al. (Ref. 27) showed that cracked jet fuels are less stable in storage than are straight-run fuels; that copper but not steel surfaces increase deposition rates; and that polysulfides, mercaptans, and thiophenol all promote deposit formation while nitrogen compounds have little effect. Thompson, et.al. (Ref. 23,24) reported similar results but included nitrogen compounds among the deposit-promoters. Taylor and Frankenfeld (Ref. 28) have demonstrated the detrimental influence of pyrroles at high concentrations and confirmed an earlier report (Ref. 29) of increased deposition rates when the fuel is exposed to sunlight (Ref. 29).

Thermal stability, the resistance to formation of deposits on heated surfaces in an operating jet aircraft engine, is an important performance parameter. Olefins have been reported as very active deposit-forming species (Ref. 30-34) while naphthenes have been variously labeled as deposit-promoters (Ref. 35-38) and deposit-inhibitors (Ref. 30,39). Numerous studies attest to the importance of molecular oxygen in thermal stability (Ref. 39-44). However, Taylor has demonstrated that deposits do form even in the absence of oxygen (Ref. 33). The deposits formed under these conditions differ in composition from those produced in the presence of oxygen. Further, in deoxygenated fuels the addition of a peroxide, acid, ester, or ketone decreases stability. Alcohols and phenols are less harmful and ethers have little effect. Nitrogen compounds generally decrease stability (Ref. 45-47). At very high pyrrole concentrations, the resulting deposits consist of oxygenated polymerization products ("pyrrole-black") (Ref. 47,48). Similarly, thiols, sulfides, disulfides, and thiophenes have been reported to decrease thermal stability (Ref. 30,31,49-52). The effect has been attributed to free-radical initiation (Ref. 52). Metal surfaces and dissolved metal salts can also decrease stability (Ref. 53,54).

Therefore, a considerable mass of observation on the dependence of fuel stability on the composition of the fuel has been collected. However, systematic quantitative data suitable for mechanistic studies are lacking. The experimental approach taken in this investigation was therefore designed to permit observation of the effect of variation of a single parameter on a quantitative measure of fuel stability. The following specific studies were conducted:

1. Development and testing of non-standard methods for measurement of both dissolved and deposited gums in turbine fuels.

2. Determination of the influence of coal-derived Lewis bases on the rates of formation of dissolved and deposited gums in Jet A fuel and on JFTOT (Jet Fuel Thermal Oxidation Tester) results for the fuel.
3. Investigation of the influence of twenty-three individual nitrogen heterocyclic compounds on deposited gum formation in Jet A and Diesel fuels. Temperature and concentration effects were considered.
4. Fractionation of Diesel fuel via adsorption chromatography and evaluation of contributions of the fractions to deposit formation.
5. Study of the influence of free-radical initiators on deposit formation in Jet A.
6. Kinetic study of tetralin autoxidation in dodecane solution.
7. Determination of the effect of nitrogen heterocycles on deposit formation in tetralin/dodecane (1/10 V/V).
8. Development of a high performance liquid chromatography (HPLC) method for analysis of tetralin hydroperoxide and its decomposition products in dodecane solution.
9. Study of the effects of nitrogen heterocycles on the rates of formation and decomposition of tetralin hydroperoxide in dodecane solution.
10. Investigation of the effects of adding tetralin hydroperoxide, tetralone, and tetralol on deposition in Jet A.
11. Evaluation of the effects of thiols, thiophenes, sulfides, and disulfides on deposit formation in Jet A.
12. Study of the effect of Cu metal and copper acetylacetonate on deposition in Jet A.
13. Development of an HPLC technique for monitoring production of deposit precursors.
14. Evaluation of the use of fuel dielectric constant as an indication of fuel degradation.
15. Study of changes in composition of nine synfuels upon thermal stressing.
16. Characterization of deposits from Jet A and from tetralin/dodecane using a variety of instrumental analysis techniques.

EXPERIMENTAL WORK

The experimental work reported, except JFTOT measurements, was conducted in the laboratories of the Department of Chemistry and Geochemistry, Colorado School of Mines, Golden, Colorado. The JFTOT tests were performed at the National Aeronautics and Space Administration Lewis Research Center, Cleveland, Ohio.

Chemicals and Materials

Fuels. A single batch of commercial Jet A, acquired from the Lewis Research Center, was employed for all Jet A accelerated storage stability tests. A second batch was used for JFTOT measurements. All experiments on Diesel fuel stability were performed using a single batch of a 533-589°K (500-600°F) cut of Texaco D454. Both fuels, stored at 277°K (40°F), were filtered through a fine, sintered-glass funnel immediately before use.

The synfuels tested, obtained from the Lewis Research Center, were prepared by Atlantic Richfield Company (Ref. 54). Of the nine synfuels tested, eight were derived from oil shale and one from coal. These samples had been stored in clear, glass bottles for several years. They were filtered prior to use.

The model "fuel" studied consisted of a 1/10 (V/V) solution of tetralin in n-dodecane. The n-dodecane was washed with concentrated H_2SO_4 until the H_2SO_4 layer was colorless, then once with dilute aqueous NaOH, and finally with deionized water. The washed dodecane was then distilled, and the purity of the distillate was verified by gas chromatography and UV (ultraviolet) spectroscopy. Tetralin was also distilled prior to preparation of the model "fuel".

Extract. A Lewis base extract from a Utah A-seam coal syncrude was prepared via batch ligand-exchange. Amberlite IRC-50 was dehydrated by Soxhlet extraction with dry tetrahydrofuran (THF), converted to the Fe(III) form with saturated $FeCl_3$ in THF, and washed free of chloride ion with dry THF. A filtered solution of 150 ml coal liquid in 100 ml dry THF was equilibrated with 100 ml of the resin in the Fe(III) form. Uncomplexed components were removed by Soxhlet extraction with dry THF. Complexed ligands were then displaced from the resin with saturated NH_3 in THF, and the solvent was removed via rotovaporation (10 torr, 60°C).

Reagents. Pyrrole was purchased from Matheson, Coleman, and Bell; 2,6-dimethylquinoline, quinoline, 8-hydroxyquinoline, chloroform, isooctane, and all organic sulfur compounds from Eastman Organic Chemicals; THF and acetonitrile from Waters Associates; tetralin, tetralone, n-dodecane, and the other organic nitrogen compounds used from Aldrich Chemical Company.

Liquid nitrogen and sulfur compounds were distilled prior to use; solids were used without further purification.

Tetralin and decalin hydroperoxide were prepared by the method of Knight and Swern (Ref. 57). Tetralol was prepared by reduction of 40.0 g tetralone with 5.0 g $LiAlH_4$ in 100ml THF. After two hours at reflux, the mixture was cooled, hydrolyzed with 200ml 10% H_2SO_4, and saturated with NaCl. The THF layer was separated and dried over $MgSO_4$. After roto-vaporization of THF, 35.0 g of a 55/45 mixture (determined by proton NMR) of tetralol/tetralone remained. The crude product was dissolved in 200 ml 95% ethanol and reacted with 15.0 g semicarbazide hydrochloride and 22.5 g sodium acetate for one hour at 70°C. After filtration, the solvent was removed by roto-vaporization. The slightly-yellow oil (18 g) shows no carbonyl band in the infrared spectrum.

Copper acetylacetonate($Cu(acac)_2$), synthesized according to (Ref. 58), was recrystallized from acetone. Copper metal foil (.002", Sargent-Welch) was used without any treatment.

Analytical Methods

Gas chromatography (GC) was performed with a Varian 3700 gas chromatograph equipped with FID (flame ionization detector) and AFID(alkali flame ionization detector). Model system analyses and monitoring of compound purity were conducted using a 6' X 1/8", 3% Carbowax 20M on Teflon column. Analyses of the Lewis base extract and of polar constituents employed a 6' X 1/8", 3% Dexsil 300 on Chromsorb W column. The AFID provided nitrogen-selective detection. A Perkin-Elmer 270 mass spectrometer was used for GC/MS (gas chromatography/mass spectrometry) analyses.

A Waters Associates liquid chromatograph fitted with Model 6000 constant flow pumps, Model U6K syringe-loading injector, a Model 440 UV detector (254 nm), and a Model R401 refractometer provided HPLC analyses. Normal phase separations were performed using a Waters Associates μ-Porasil column. Gel permeation chromatography was carried out using series-connected ¼" X 20" columns slurry-packed with Bio-Beads S-X8 and S-X12; the elution solvent was THF at a flow rate of 0.5 ml/min.

Infrared spectra were recorded using a Perkin-Elmer Model 521 IR Spectrophotometer. Multiple internal reflectance (MIR) spectra were obtained using a Wilks Model 9 MIR attachment. Spectra in the UV region were obtained with a Beckman DK-2A Spectrophotometer. Absorbance measurements at selected wavelength were made on a Beckman DU Spectrophotometer.

Dielectric constants were measured with a Sargent Model V Chemical Oscillometer. Expansion of the oscillometer scale was achieved by adding inductance with a Sargent S-29196 Oscillometric Cell Compensator.

Elemental analyses were obtained using a Carlo Erba Model 1104 Elemental Analyzer. Weight measurements were made using a Cahn Model 4700 Electrobalance. Liquid samples were placed in crimped indium capillaries for introduction into the combustion zone.

Secondary-ion mass spectrometry was performed by Dr. Robert Orth at the Department of Chemistry, University of Utah, Salt Lake City, Utah. For all spectra, the primary ion was 2.0 KeV Ar^+.

Thermal stability determinations were made using the JFTOT apparatus (Alcor, Inc.) at the Lewis Research Center. The deposits were rated using the Alcor Mark 8A tube deposit rater.

Gum Determinations

The "dissolved gum" content of fuel samples was determined by filtration of the fuel through a fine, sintered-glass funnel and rapid evaporation of a one-ml aliquot under vacuum (approximately 5 minutes at 9 torr and ambient temperature). The residue weight was taken as representative of the amount of "dissolved gum". These results are not intended to be equivalent to values obtained by ASTM D837-57T or other standard methods.

"Deposited gum" produced during storage stability tests was determined by weighing the deposit adhering to a tared 18 X 18 mm glass coverslip placed in the bottom of the sample container during the storage period. Prior to weighing, the small amount of adsorbed fuel was evaporated from the coverslip using a IR lamp (approximately 5 minutes). Results are not directly comparable to standard methods. Where results are reported in mg/mm^2, the area used is 324 mm^2.

Stability Tests

The experimental protocol was not designed to provide absolute measurement of fuel stability or measures necesarily related to ASTM methods, but to permit reasonably rapid and reproducible comparisons of stabilities of small samples of fuels differing slightly in a single compositional parameter.

Jet A, Storage. Flint glass jars of 147 ml capacity were cleaned for 48 hours in chromic acid solution; then rinsed and placed in sodium bisulfide solution for 24 hours to reduce Cr(VI) to Cr(III) and facilitate its removal from the glass surface.

Finally, the jars were rinsed repeatedly with deionized water and allowed to air dry. A tared coverslip was placed in each jar followed by 10.0 ml of fuel. The jar was sealed with a screw cap lined with PTFE sheet, and then placed in an oven at 394°K (250°F).

Each 24 hours, three samples were removed, cooled, and analyzed for both dissolved and deposited gum. The results are shown in Figure 1. The reproducibility of each method was evaluated by replicate measurements (Tables 1 and 2). The possible influence of the jar cleaning procedure on the results was also studied by parallel replicate runs using new, uncleaned jars; new, cleaned jars; and previously used, cleaned jars (Table 2).

Extract-spiked Jet A, Storage. A weighed quantity of analyzed extract was dissolved in THF and diluted to known volume. That volume of the extract solution required to produce the desired nitrogen concentration was transferred, by means of a micropipet, to a clean jar. Then 10.0 ml Jet A was pipetted into the jar; a coverslip was introduced; the jar was sealed with PTFE-lined screw-cap; and placed in the oven at 394°K. Analyses of both dissolved and deposited gums were performed after 144 hours of aging.

To assess the influence of the THF solvent on the fuel stability, three blanks were run to which 1.0 ml THF (at least ten-fold the amount introduced in the extract spiked fuels) rather than extract solution was added (Table 3).

Extract-spiked Jet A, Thermal. Two 600-ml samples of Jet A were spiked with the Lewis base extract at a concentration of 20 ppm N. These samples and two 600-ml samples of Jet A (unspiked) were then aged for 144 hours at 394°K. These four samples and four samples of unaged Jet A, to two of which Lewis base extract (20 ppm N) was added just prior to testing, were subjected to JFTOT analysis. For each test, the apparatus was operated at 533°K (500°F). For each test, the maximum tube rating was determined (Table 5).

Compound-spiked Jet A, Storage. Standard solutions of individual compounds in THF were prepared. The appropriate volume of solution to impart the desired concentration in the fuel was introduced into a jar using a micropipet. A coverslip and 10.0 ml Jet A were added; the jar was sealed; and the sample was aged as above.

Diesel, Storage. The aging procedure was analogous to that used for Jet A. In addition, however, a 300-ml batch of the Diesel fuel was fractionated. The fuel was slurried with approximately 200 ml silica gel (Baker 3405 activated 24 hours at 673°K). The treated fuel was then removed by vacuum filtration. The silica gel was then washed successively with three 100-ml portions each of hexane, toluene, chloroform, and THF. After each washing, the extract was removed by vacuum filtration. The three portions of each solvent were combined and the solvent was removed by roto-vaporation.

The four resulting extracts were each dissolved in 10 ml THF. Ten-ml samples of the silica-gel-treated Diesel were spiked with 0.67 ml of extract (twice the level removed) and 10-ml samples of untreated Diesel were spiked with 0.33 ml of extract. In addition, an appropriate volume of a standard quinoline in THF solution was added to some of the samples (5 ppm N added). These samples were aged as before.

Model, storage. The aging procedure used was that above for Jet A except that the coverslip was not placed in the sample jar. Rather, the amount of deposit was determined by decanting the "fuel" from the container, rinsing the container with benzene, allowing to air dry, and weighing the bottle plus adhering deposit. In addition, one-microliter samples of the solution phase were analyzed by GC and HPLC at 24 hour intervals during aging.

In addition to experiments in which the model fuel was spiked with nitrogen heterocycles (by the procedure used with Jet A), runs were also made with the addition of tetralol, tetralone, tetralin hydroperoxide, and various combinations of these and the nitrogen compounds to the model "fuel".

Synfuels, Storage. The procedure was that used for Jet A.

Deposit Characterization

Samples of the deposits produced in the accelerated storage tests were subjected to the instrumental analyses described above. Fuel was decanted from the container; the adhering deposit was rinsed with hexane and then allowed to air dry; finally the deposit was mechanically dislodged from the glass surface with a stainless steel spatula.

A thermal deposit produced in a simulator at the Lewis Research Center was used for SIMS analysis. The deposit was formed on aluminum foil at 500°F by the flow of 700 ml of Jet A across the Al surface. The surface was heated from ambient to 500°F in $\frac{1}{2}$ hour; maintained at 500°F for 2 $\frac{1}{2}$ hours; and was cooled to ambient in $\frac{1}{2}$ hour.

Larger quantities of sample were also obtained by passing a filtered air stream through fuel in a heated flask. The deposit was collected by filtration, washed with hexane, and air dried. Material adhering to surfaces was dislodged and included.

Characterization of Aged Fuel

The effect of accelerated storage on the composition of the fuels was studied by monitoring various properties during the aging process. Generally, the sample container was removed each 24 hours and allowed to cool to ambient temperatures. The container was opened and the desired measurement (absorbance at 340 nm, GC, HPLC, dielectric constant, refractive index) made. The fuel sample was then returned to the same container and returned to the oven.

RESULTS AND DISCUSSION

Method Development

Investigation of reaction mechanism in a system as complex as a turbine fuel is most readily approached by single parameter variation. The large number of independently variable composition parameters therefore required the use of a single batch of fuel. Further, replicate determinations are necessary to verify acceptable control of parameters. Therefore, evaluation methods were required which provide rapid, reproducible, relative stability data on small samples. The accuracy of the methods, in terms of performance specifications, was not of concern. The two techniques developed for monitoring storage stability are not, therefore, intended to yield data comparable to standard methods (Ref. 59).

A number of methods for evaluation of fuel degradation were explored and found unsatisfactory for the purposes of this investigation. Light transmittance at 350 nm (Ref. 60) gave poor reproducibility and absorbance increased too rapidly. Direct weighing of deposited gum was impractical due to distribution of the material between suspension and very strong adhesion to surfaces. Relative insolubility precluded extraction as a collection means. Evaporation of filtered fuel at atmospheric pressure and 373°K in a stream of N_2 proved too time-consuming for dissolved gum determination. The reproducibility of the methods used is illustrated by the data of Tables 1 and 2.

TABLE 1. REPRODUCIBILITY OF THE "DISSOLVED GUM" METHOD
(Fuel aged 10 days at 394°K, units are g gum/ml x 10^5)

Sample	Unaged Jet A	Aged Jet A
1	13	19
2	14	20
3	12	18
4	16	22

TABLE 2. REPRODUCIBILITY OF THE "DEPOSITED GUM" METHOD
(g gum/mm^2 x 10^7 in Jet A + Quinoline (5ppmN), 7 days at 394°K)

Containers	Deposit Density	Average	Average Deviation
New	9.9,11.1,11.7,11.1,12.7	11.3	0.7
New, Cleaned	8.3,9.0,13.9,13.3,13.0,14.2	12.0	2.2
Used, Cleaned	10.5,9.6,9.9,10.8,13.9	10.9	1.2

The effective precision of the methods is also a function of the extent of aging. In initial stages of deposit formation precision is poor on a relative basis. After extensive deposition, however, some deposit becomes suspended in the fuel rather than collecting on surfaces (Figure 1). Therefore, an aging time of 6 days (144 hours) was used in the initial stability experiments. This was increased to 7 days (168 hours) in the later experiments to increase sensitivity to small differences.

In recognition of the range of surface effects on stability which have been reported (Ref. 30), possible bias in the results arising from the procedure used to clean sample containers was investigated. As the data of Table 2 attest, no significant influence was found. However, when PTFE cap liners were used a second time, much higher, erratic deposition rates resulted. Hence, cap liners were replaced for each run.

The effect of THF (the solvent used in spiking fuel samples) on fuel stability was also assessed. Addition of one ml THF to ten ml Jet A did not significantly alter deposited gum values while dissolved gum results were lowered somewhat (Table 3). These results are rather surprising. THF readily forms a hydroperoxide (Ref 60) and the formation of hydroperoxides has been suggested as the initiation process in the formation of fuel deposits (Ref. 61).

TABLE 3. EFFECT OF THF ON JET A STABILITY
(Fuel aged for 8 days at 394°K)

Dissolved Gum, g/ml x 10^5		Deposited Gum, g/mm^2 x 10^7	
Jet A	Jet A + THF	Jet A	Jet A + THF
26	17	0.6	0.6
21	15	0.6	0.4
17	12	0.6	0.4

The lack of acceleration by THF may reflect a rapid loss via volatilization. In any event, the addition of small volumes (<<1ml) of THF in spiking experiments was considered acceptable.

While several methods have been used for the extraction of bases from petroleum and similar materials (Ref. 62-65), the technique used here produces an extract relatively free of non-bases and avoids the complications inherent in treating the sample with mineral acid. Extensive extraction of the complexed resin (to remove non-bases) doubtless resulted in displacement of some bases by THF. Use of an extraction solvent of lower basicity toward Fe(III) would likely increase the yield (about 25% based on nitrogen analyses). Indeed, we have obtained much higher yields using Cu(II) sites and methanol as extraction solvent (Ref. 55). The requirement here was an extract containing a representative range of Lewis bases found in syncrudes. A large variety of nitrogen compounds were identified based on GC and GC/MS analysis of the extract.

The composition of the extract was reasonably constant for separate preparations (Table 4). The variation may result from inhomogeneity of the syncrude rather than from irreproducibility of the extraction process.

TABLE 4. COMPOSITION OF LEWIS BASE EXTRACT
(Retention times of the major GC peaks in minutes for 3% Dexsil 300 on Chromosorb W, temperature programmed from 150°C to 250°C at 10°C/min)

Batch 1	Batch 2	Batch 3	Standards
-	-	3.21	
-	-	4.15	
5.21	5.20	-	indoline 5.20
6.08	6.07	6.07	quinoline 6.00, indole 6.15
6.62	6.62	6.53	tetrahydroquinoline 6.64
-	-	7.13	2-methylindole 7.30
7.53	7.50	7.53	2,6-dimethylquinoline 7.78
8.03	7.95	8.11	
8.68	8.62	8.66	
-	9.10	9.19	
10.74	10.70	-	
-	11.10	-	
11.40	11.35	11.40	7,8-Benzoquinoline 11.23
11.73	11.76	11.70	Carbazole 11.53
-	12.00	-	

Nitrogen content of the extracts was 3.35-3.50% N after removal of solvent.

Extract-Spiked Jet A

Addition of the Lewis base extract to Jet A decreases the storage stability of the fuel (Figures 2 and 3). The extent of gum formation (144 hours, 394°K) increases with the amount of extract added (expressed as ppm N added). The concentration of "dissolved gum" becomes essentially constant above 200 ppm N added. Since there is no concurrent discontinuous increase in deposition, this does not appear to represent saturation of the fuel with "dissolved gum". Perhaps, saturation of the solution phase with extract at that level and the restriction of deposit-promotion to solution-phase components is indicated.

The JFTOT analyses of extract-spiked Jet A before and after aging were of such poor reproducibility as to provide little information (Table 5). The volume of fuel required (ca. 600 ml per determination) preclude the use of JFTOT in mechanistic studies. Homogeneity problems, both with respect to fuel and extract, are limiting.

TABLE 5. JFTOT RESULTS ON EXTRACT-SPIKED JET A
(20 ppm N added, samples aged 144 hours at 394°K,
the JFTOT apparatus was operated at 533°K)

Sample	Maximum Tube Rating
Jet A	9.0, 2.5
Jet A + extract	9.0, 9.0
Jet A, aged	6.0, 2.0
Jet A + extract, aged	3.0, 9.0

Although extract concentration was specified in terms of added nitrogen content, Lewis bases other than nitrogen compounds are undoubtedly present as well. Phenols form strong Fe(III) complexes, for example. Therefore, the reasonableness of using individual nitrogen compounds was assessed by comparing their effect on stability to that of the extract at comparable nitrogen concentration. The compounds selected are all nitrogen heterocycles representative of the predominant types found in coal and oil shale materials. The resulting deposited gum values are comparable to that obtained for the extract (ca. 5.3 at 5 ppm N added from interpolation in Figure 2) as shown in Table 6.

TABLE 6. EFFECT OF VARIOUS NITROGEN COMPOUNDS ON
DEPOSITION IN JET A.
(50 mg compound/liter fuel, samples aged 6 days at 394°K)

Compound Added	ppm N added	g deposit/mm^2 x 10^7
Quinoline	5.42	3.6
Carbazole	4.18	3.7
Indole	5.97	6.2
2,6-Dimethylquinoline	4.45	10.2
7,8-Benzoquinoline	3.91	3.7
2-Methylindole	5.43	8.6
Indoline	5.87	7.2
2-Acetylpyridine	5.78	9.2
Pyrrole	10.43	7.2
2-Pyrrolidone	8.22	7.2

While other constituents of the extract may also influence deposition rates, nitrogen heterocycles appear to be reasonable model compounds for studying the effects of fuel bases on stability.

Nitrogen-Heterocycle-Spiked Jet A

Four classes of compounds, each found in petroleum-, coal-, and oil shale-derived materials (Ref. 66,67), were selected for study: pyrroles, indoles, pyridines, and quinolines. A number of compounds in each class, providing a range of electronic and structural environments at the nitrogen, is commercially available in reasonable purity.

The acceleration of deposition as a function of added nitrogen concentration was determined for the four parent compounds (Figure 4). Pyridine and quinoline (heterocycles in which nitrogen contributes one electron to the pi system) produce strongly concentration-dependent, increased deposition. Indole and pyrrole (heterocycles in which nitrogen's nonbonding electron pair participates in the pi system) produce only a small enhancement with little concentration dependence. If the weight of deposit is assumed to be proportional to the specific reaction rate, Figure 4 suggests first-order dependence for pyridine and quinoline and nearly zero-order for pyrrole and indole. Mechanistic differences are suggested in the two cases.

The ineffectiveness of pyrrole in promoting deposition is in apparent contradiction to previous reports (Ref. 24,28). In those studies, very high concentrations of pyrrole caused deposition of "pyrrole black". Here, the weight of added pyrrole (even at the highest concentration level) would not represent a significant contribution to the total weight of deposit which formed. Furthermore, elemental analyses of the deposits did not show any significant nitrogen enrichment. However, examination of the deposits under the microscope revealed marked differences in appearance. Deposits from pyrrole- and indole-spiked Jet A consist of small, black "solid" particles while deposits from pyridine- and quinoline-spiked Jet A consist of larger, black, "solid" particles plus a viscous, amber "liquid". The temperature at which deposition occurs also influences the appearance. At higher temperatures, the particle size increases as does the proportion of amber "liquid" present. The form apparently depends upon rate of deposition, the amber form

TABLE 7. ELEMENTAL ANALYSES OF DEPOSITS
(Triplicate analyses, spiking of fuels at 5 ppm N added)

Fuel Sample	% C	% H	% N
Jet A	69.3 ± .2	5.3 ± .2	.25 ± .01
Jet A + pyrrole	72.5 ± .2	4.99 ± .02	.25 ± .01
Jet A + indole	72.5 ± .1	5.19 ± .05	.22 ± .02
Jet A + pyridine	72.4 ± .1	5.37 ± .07	.28 ± .03
Jet A + quinoline	71.4 ± .4	5.12 ± .06	.31 ± .02

predominating when deposition is rapid.

The variation in effectiveness of individual nitrogen compounds in promoting deposition was studied further by spiking Jet A with 23 different compounds. In all cases, the quantity of compound added was equivalent to 5 ppm N added (3 x 10^{-4}M). This level produced appropriate quantities of deposit on the coverslips in 168 hours at 394°K for the collection of compounds (Table 8).

TABLE 8. EFFECTS OF PYRROLES, INDOLES, PYRIDINES, AND QUINOLINES ON DEPOSITION FROM JET A
(5 ppm N added, aged 168 hours at 394°K)

Compound Added	(g deposit/mm^2) x 10^7	pKa (Ref. 68)
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	5.2
7,8-Benzoquinoline	2.8 ± .5	4.3
4-Hydroxy-2-methylquinoline	9.1 ± .4	--
8-Hydroxyquinoline	8.1 ± .2	4.91

The influence of a given compound on deposition rate is clearly not determined solely by the class to which the compound belongs. In Figure 5, the effectiveness in promoting deposition and basicity (as represented by the pKa of the aqueous conjugate acid) are compared. Good correlations result within the four compound classes (correlation coefficients are: .96 quinolines, .97 indoles, .92 pyridines) but not for the entire suite of compounds as a whole. The correlation coefficient for pyridines was calculated with omission of the value for 2,4,6-trimethylpyridine. The low deposition rate produced by this compound and the similar result for 1,2,5-trimethylpyrrole suggest the importance of steric hindrance at the nitrogen atom.

If the deposit weight per unit area is taken as proportional to the specific rate, then the linear correlations of Figure 5 are consistent with the Bronsted equation for general base catalysis (ref. 69).

$$\text{Log } k = \text{constant} = \beta \text{pKa} \quad (0<\beta<1 \text{ for pKa of the aqueous conjugate acid})$$

The lack of correlation for all classes taken together suggests the influence of electronic factors other than those determining basicity. Addition of benzenoid nuclei (e.g. pyridine → quinoline → benzoquinoline) causes large changes in effectiveness as does removal of the nitrogen from the pi system (e.g. indole → indoline).

The coverslip method restricts determinations to a rather small range of deposit weights and hence to a small range of deposition temperatures. Deposition rates over the temperature range 382-405°K (228-271°F) for Jet A spiked with the four parent compounds (5 ppm N added) are compared in Figure 6. Again, if deposit weight is assumed proportional to specific rate, then Figure 6 may be interpreted as an Arrhenius plot. The linearity of the plots and of a plot of Arrhenius slope versus intercept (Figure 7) indicate uniformity of mechanism. The linear relationship of slope and intercept may represent an isokinetic relationship (Ref. 70) or simply arise from the assumptions made or from experimental error. However, a plot of Exner's transformation co-ordinates (Ref. 71) is also linear (Figure 8) lending more support to the presence of the isokinetic effect and to the assumption that deposit weight is proportional to the specific rate. The energy of activation can increase as specific rate increases (as Figure 6 would indicate) when experimental temperatures are above the isokinetic temperature and entropy effects are controlling (Ref. 71-74). However, in a system of this complexity with data over a limited range, this interpretation is highly speculative.

The suggestion that the reaction is entropy controlled is supported to some extent by the Bronsted plot (Figure 5). A small slope of the Bronsted plot indicates proton transfer early in the transition state and a large slope corresponds to late proton transfer. A slope between zero and one is interpreted as indicative of simultaneous proton transfer and nucleophilic attack (Ref. 75-77). The slopes from Figure 5 are: pyrroles 1.02, indoles 0.27, quinolines 0.67, and pyridines 0.74. To the extent that application of the Bronsted Law is valid here, the involvement of substrate, base, and nucleophile in the transition is indicated (Ref. 77). Such a transition state should require high activation entropy.

Nitrogen-Heterocycle-Spiked Diesel Fuel

The effects of nitrogen heterocycles on Jet A were all observed using a single batch of Jet A. Hence parallel studies with a fuel of different composition were undertaken to verify that the effects are not peculiar to the single fuel sample. The Diesel studied is considerably higher in aromatics than is the Jet A sample (Figure 9 and 10) and has a higher dielectric constant (Diesel 2.342, Jet A 2.129). The effects of the nitrogen heterocycles (at 5 ppm N added) on the Diesel are given in Table 9. The correlation of the effects with basicity is also demonstrated in Figure 11. Despite the compositional difference between the two fuels and the higher deposition rates in the Diesel, the nitrogen compound effects are very similar (Figure 12). The promotion of deposit formation by the nitrogen compounds is generally greater in the Diesel fuel (Table 10). Perhaps enhancement of basicity in the medium of higher dielectric constant (Diesel) is responsible.

Higher absolute deposition with Diesel suggests the presence of higher concentrations of reactive fuel components or of trace materials which catalyze deposition. Fractionation of the Diesel provided a method for identification of these active components. The technique used was a modification of the procedure developed by Schiller and Mathiason (Ref. 78) for separation of coal-derived materials. The predominant components in each fraction are: hexane-aliphatics, toluene-aromatics, chloroform-ethers and nitrogen compounds, and THF-highly polar compounds.

The silica-treated fuel is much more stable. The effects on stability of adding back the extracted fractions are shown in Figure 13. In each case, the first bar represents control fuel (silica-treated Diesel in A, silica-treated Diesel + quinoline (5 ppm N) in B, untreated Diesel in C, and untreated Diesel + quinoline in D). The second bar corresponds to control fuel + toluene extract, the third to control + chloroform extract, and the fourth to control + THF extract. The toluene and chloroform extracts show some influence. However, the resulting fuel is more stable than untreated Diesel although the extract was added back at twice the level removed. In addition, quinoline has little effect. Components of the THF extract, by contrast, have a pronounced effect which is abetted by quinoline.

The stability of Diesel fuel is thus strongly dependent upon the highly-polar components and the acceleration of deposit formation by nitrogen compounds requires the presence of these highly-polar components. The nitrogen compounds do not significantly catalyze the formation of the required polar constituents from non-polar fuel compounds (compare the first bars in A and B with those in C and D). Their effect appears to be catalysis of reactions leading to intermediates which react with polar fuel components.

TABLE 9. EFFECTS OF PYRROLES, INDOLES, PYRIDINES, AND QUINOLINES ON DEPOSITION FROM DIESEL (5 ppm N added, aged 168 hours at 394°K)

Compound added	g deposit/mm^2 x 10^7	pKa
Control (no spike)	8.0 ± .2	-
Pyrrole	19.6 ± 3.6	-3.8
N-Methlypyrrole	34.9 ± .3	-2.90
2-Pyrrolidone	20.7 ± 3.5	-
1,2,5-Trimethylpyrrole	15.1 ± 3.5	-.24
Indole	19.6 ± .2	-2.4
N-Methylindole	21.3 ± 3.2	-1.80
2-Methylindole	22.9 ± 3.8	-.10
3-Methylindole	17.3 ± 3.1	-3.35
Indoline	19.1 ± .8	-
N-Ethylcarbazole	23.5 ± .2	-
Pyridine	21.9 ± 2.3	5.22
2-Acetylpyridine	21.0 ± 4.6	-
2-Methylpyridine	13.6 ± .8	5.94
4-Methlypyridine	17.0 ± .6	6.03
2-Ethylpyridine	11.8 ± .9	5.93
2,6-Dimethylpyridine	18.7 ± 4.8	6.64
2,4,6-Trimethylpyridine	18.1 ± 2.1	7.43
Quinoline	15.8 ± 1.2	4.85
2,4-Dimethylquinoline	21.5 ± .9	5.12
7,8-Benzoquinoline	15.1 ± 1.0	4.3
8-Hydroxyquinoline	17.2 ± .1	4.91

TABLE 10. EFFECTIVENESS OF DEPOSIT PROMOTERS IN DIESEL AND JET A

Compound	% Increase in deposit over control	
	Jet A	Diesel
Pyrrole	3	145
N-Methylpyrrole	156	336
2-Pyrrolidone	24	159
1,2,5-Trimethylpyrrole	9	89
Indole	12	145
N-Methylindole	6	166
2-Methylindole	103	186
3-Methylindole	-32	116
Indoline	97	139
N-Ethylcarbazole	29	194
Pyridine	6	174
2-Acetylpyridine	3	163
2-Methylpyridine	132	70
4-Methlypyridine	159	113
2-Ethylpyridine	73	48
2,6-Dimethlypyridine	194	134
2,4,6-Trimethlypyridine	38	126
Quinoline	126	98
2,4-Dimethlyquinoline	141	169
7,8-Benzoquinoline	-18	89
8-Hydroxyquinoline	138	115

Silica treatment of Jet A similarly increases the stability. HPLC clearly shows the removal of polar materials by silica treatment for both fuels (Figures 14 and 15). These analyses were performed on µ-Porasil using a 65/35 (V/V) isooctane/chloroform mobile phase which is 0.1M in acetonitrile. The flow rate was 2 ml/min and the UV detector (254nm) was employed.

Radical-Initiator Studies

The apparent involvement of polar constituents and the correlations of deposit promotion with basicity argue for an ionic transition state or, at least, a transition state with substantial charge separation. The increased deposition in Diesel may even represent increased solvation of the transition state in the medium of higher dielectric constant. Many investigators have attributed fuel instability to free-radical reactions (Ref. 8,9,10,79). Therefore, the effects of spiking

Jet A with azobisisobutyronitrile and with benzoyl peroxide (radical initiators at the deposition temperature) were investigated. As is shown in Table 11 the initiators do cause earlier onset of deposition but do not increase the absolute amount of deposit formed in the usual 7 day test period. Indeed benzoyl peroxide reduced deposit weight. The lack of increase in deposit is not consistent with the operation of a free-radical mechanism of deposition under these conditions.

TABLE 11. EFFECT OF RADICAL INITIATORS ON DEPOSITION (quinoline (Q) at 3.6 x 10^{-4}M, azobisisobutyronitrile (ABIN) at 8.9 x 10^{-3}M, benzoyl peroxide (BP) at 1.6 x 10^{-2}M. Amount of deposit reported in g/mm^2 x 10^7).

Days	Jet A	Jet A + Q	Jet A + ABIN	Jet A + BP
1	-	.21	1.44	1.34
2	-	4.94	2.37	1.03
3	.31	6.50	2.57	1.03
4	.52	6.18	3.50	1.75
5	2.00	6.68	3.48	1.23
6	3.40	6.50	3.69	1.54
7	3.40	7.71	3.50	1.54

Model Fuel Development

Detailed mechanistic studies in systems as complex as the Jet A or Diesel fuels is enormously hampered by the very large number of potential reactants present. Thus, a model "fuel" containing the minimum number of components which mimicks the deposition behavior of the true fuels was sought. Clearly the major constituents of these fuels are hydrocarbons. For the model fuel, n-dodecane was selected as an appropriate hydrocarbon medium of reasonable boiling point (488°K).

As stated earlier, autoxidation is widely-believed to be the initial process in deposit formation in gasoline (Ref. 14). Elemental analyses of deposits (Table 7) suggest the presence of large amounts (ca. 25%) of oxygen. Therefore, tetralin was included in the model fuel due to its ready autoxidation, and naphthenic character. The autoxidation of tetralin has been extensively studied in both gas and solution phases. The process has been shown to be first-order in tetralin in both cases (Ref. 80,81,82).

Since study of the kinetics of tetralin autoxidation in dodecane solvent had not been published, verification of first-order kinetics was undertaken. The rate of tetralin consumption in a 10/1 (V/V) n-dodecane/tetralin solution was monitored by GC at three different reaction temperatures. As is exhibited in Figure 16, the reaction is first order in tetralin. The calculated activation energy of 20.7 kcal/mole compares favorably with reported values in other media (Ref. 83-87). Therefore, the reaction is undoubtedly a free-radical process analogous to that reported for autoxidation of neat tetralin (Ref. 87).

When aged at 394°K for 220 hours, in the same manner as Jet A was aged, the tetralin/dodecane (1/10, V/V) model "fuel" produces deposits very similar in appearance to those obtained with Jet A. The influence of pyrrole, indole, pyridine, and quinoline (10 ppm N added) on total deposit weight produced is, likewise, similar to that on Jet A (Fig. 17). This increased deposit formation is not the result of increased autoxidation of tetralin as shown in Figure 18.

Tetralin hydroperoxide, the primary tetralin autoxidation product, decomposes rather easily. Among the decomposition products are tetralol and tetralone (Ref. 88-90). To monitor these decompositon reactions and assess their importance in the deposition process, a rapid, reliable method for the simultaneous determination of tetralin, tetralin hydroperoxide, tetralol, and tetralone was needed. Van Tilborg (Ref. 91) used gradient elution HPLC to separate ethylbenzene hydroperoxide from its decompositon products. The HPLC method developed for this study (Ref. 92) employs a single, mixed solvent (65/35 isooctane/chloroform containing acetonitrile). The separation obtained is very sensitive to the concentration of acetonitrile in the elution solvent (Figure 19). The resulting chromatogram is shown in Figure 20. Using the dodecane RI response as an internal standard, response factors were determined (Table 12).

TABLE 12. HPLC RESPONSE FACTORS
(Response factors in mole/liter/cm^2,
all correlation coefficients > .999 over
an order of magnitude)

Tetralin	Tetralone	Tetralol	Tetralin Hydroperoxide
0.32	0.042	0.064	0.027

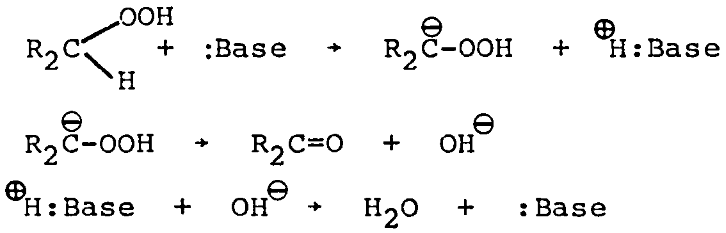
Model Fuel Mechanism Studies

The HPLC method permits monitoring of concentrations of the four compounds enabling a study of tetralin hydroperoxide decomposition. The rate of decomposition is affected by the nitrogen heterocycles as shown in Figure 21 and Table 13.

The order of effectiveness of the heterocycles is the same as that for their deposit-promotion tendencies in the model fuel, Jet A, and Diesel. The behavior in Figure 21 is consistent with the mechanism proposed by Kornblum and DeLamare for decomposition of a secondary hydroperoxide (Ref. 93):

TABLE 13. TETRALIN HYDROPEROXIDE DECOMPOSITION KINETICS
(Molarity of Tetralin Hydroperoxide in dodecane solution, 394°K, bases added at 10 ppm N concentration)

Reaction Time (hours)	Base Added				
	none	quinoline	pyridine	indole	pyrrole
0.0	.140	.140	.116	.116	.116
1.0	----	----	----	----	.103
1.5	----	----	----	.082	----
2.0	.128	.046	----	----	----
2.5	----	----	----	.066	.072
3.0	----	.034	.027	----	----
3.5	----	----	----	.048	.058
3.75	----	----	.019	----	----
4.0	.074	----	----	----	----
5.25	----	----	.009	----	----
5.75	----	----	----	.030	----
7.0	----	.006	----	----	----
8.0	.052	----	----	----	----



$$R_2C(OOH)H + :Base \rightarrow R_2\overset{\ominus}{C}\text{-}OOH + {}^{\oplus}H:Base$$

$$R_2\overset{\ominus}{C}\text{-}OOH \rightarrow R_2C{=}O + OH^{\ominus}$$

$${}^{\oplus}H:Base + OH^{\ominus} \rightarrow H_2O + :Base$$

The parallel catalysis of deposition in the model fuel and of hydroperoxide decomposition suggests the involvement of the decomposition products in deposit formation. Consequently, deposit formation in tetralin/dodecane, tetralone/dodecane, and tetralone + tetralol/dodecane was compared. The results are given in Table 14. Particularly striking is the definite

TABLE 14. MODEL SYSTEM DEPOSIT FORMATION
(Average deposit weight in grams, dodecane solutions, all catalysts added at 10ppm N)

Sample	Uncatalyzed	+pyridine	+quinoline	+indole	+pyrrole
.64M tetralin	.0638	.2676	.2212	.1310	.0704
.31M tetralone	.1545	.4197	.3703	.2520	.1412
.086M tetralone + .086M tetralol	.0025	.0032	.0026	.0025	.0025

inhibition of deposit formation by tetralol (also detected among tetralin hydroperoxide decomposition products). Tetralone is considerably more active in producing deposits than is tetralin, and the effects of the nitrogen compounds are parallel in both cases. Therefore, while catalysis of tetralin hydroperoxide decomposition certainly occurs (Figure 21), an additional influence by the nitrogen compounds must be invoked to explain the increased deposit formation from tetralone in their presence.

Tetralin-Derivative-Spiked Jet A

Tetralin hydroperoxide, tetralone, and tetralol were individually added to Jet A at a concentration of 6.1 x 10^{-5}M. The effect on deposition rate (394°K) is exhibited in Figure 22 and in Table 15.

TABLE 15. EFFECT OF OXYGEN COMPOUNDS ON JET A STABILITY (Average deposit weight in g/mm^2 x10^7)

Compound Added (6.1x10^{-5}M)	Reaction time (hours) at 394°K						
	24	48	72	96	120	144	168
Tetralin Hydroperoxide	--	2.48	3.44	4.90	5.93	6.75	6.96
Tetralone	0.93	1.90	2.84	3.30	3.62	3.36	3.53
Tetralol	0	0	0.82	0.97	2.28	2.03	2.11

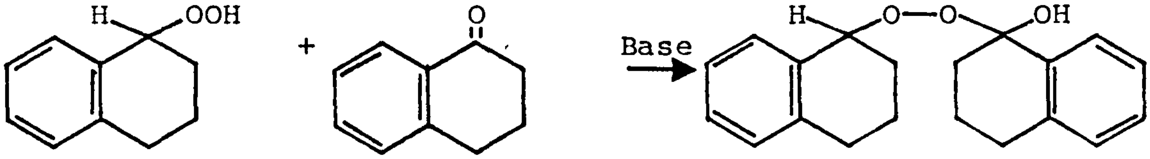
The inhibitory effect of tetralol, noted in the model system, also appears here. At this concentration level, the inhibition seems unlikely to arise from solvation phenomena and may reflect antioxidant properties of tetralol. If an induction period is granted, then the tetralol curve is quite similar to that for tetralone. In terms of absolute deposition after 7 days, the tetralone-spiked Jet A value is not greatly different from that for unspiked Jet A (2.1 x 10^{-7} g/mm^2). However, the tetralin-hydroperoxide-spiked Jet A definitely produced more deposit (6.9 x 10^{-7} g/mm^2). A role other than simple decomposition to tetralone is indicated for the hydroperoxide.

When tetralin hydroperoxide and tetralone were both added (each at ½ x 6.1 x 10^{-5}M) to Jet A, the effect on deposition was greater than for tetralone alone. Moreover, when quinoline (5 ppm N added) was also provided a very dramatic acceleration of deposition occurred (Figure 23 and Table 16).

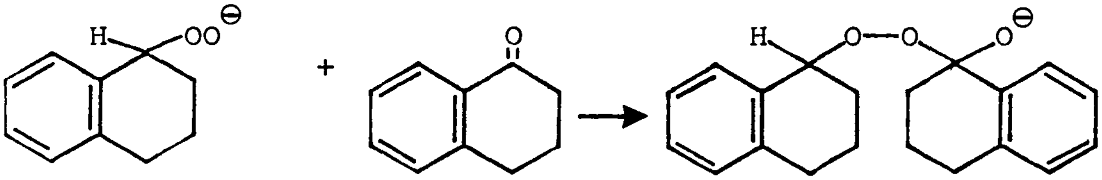
TABLE 16. COMBINED EFFECT OF OXYGEN COMPOUNDS ON JET A STABILITY (Average deposit weight in $g/mm^2 x10^7$)

Compounds Added	Reaction time (hours) at 394°K						
	24	48	72	99	120	144	168
none	1.1	1.3	2.0	2.0	1.9	1.9	2.1
Tetralin hydroperoxide + tetralone	4.9	6.2	7.4	8.4	8.2	8.9	9.3
Tetralin hydroperoxide + tetralone + quinoline	11.1	13.0	12.7	14.7	14.4	14.7	14.5

The nitrogen heterocycles evidently catalyze reactions involving both compounds which lead to deposit formation. One reasonable possibility consistent with these observations is the occurrence of a condensation of the two compounds.



In the extreme of early proton transfer, the rate-determining process becomes the nucleophilic attack



at the carbonyl carbon. In this specific base catalysis situation (Ref. 77), the ratio is independent of base concentration (approximating the situation in pyrrole- and indole-spiked fuels). In the other extreme of rate-determining proton transfer, the rate is first-order in base concentration (more closely the case in pyridine- and quinoline-spiked fuels).

Certainly, other condensation reactions (Ref. 94,95) can be postulated. Further elucidation of the mechanism requires identification of product, and if possible, intermediate compounds.

Sulfur-Compound-Spiked Jet A

Organic sulfur compounds have been reported to affect both storage and thermal stability (Ref.15,16,21,22,23,24,27,30,31,49-52). The effects on deposit formation of spiking Jet A with 11 organic sulfur compounds are presented in Table 17. While the effects are less pronounced than in the analogous experiments with nitrogen compounds significant differences between the various sulfur compounds are demonstrated. The sulfides and disulfides decrease while the other compounds promote deposition. The possibility that inhibition is due to antioxidant properties of the sulfur compounds is not supported by the results depicted in Figure 24. No evidence of an induction period is seen. Thiophenol increases deposition at the first analysis time (24 hours). Correlation of the sulfur compound effects with basicity or reduction potential is hampered by a lack of available data.

The sulfur compound effects also differ from those of the nitrogen compounds in terms of temperature dependence (Figure 25). While considerable variation between the "Arrhenius slope" values occurs for the nitrogen compounds there is very little difference among the sulfur compounds tested. Furthermore, the slope uniformly decreases as the absolute deposit rate increases. Evidently, the effect of sulfur compounds upon stability is exerted through a different mechanism than is that of nitrogen compounds despite the Lewis basicity and nucleophilicity of both.

TABLE 17. EFFECTS OF SULFUR COMPOUNDS ON DEPOSITION FROM JET A
(10 ppm S added, aged 168 hours at indicated temperature)

Compound added	g deposit/mm^2 x 10^7		
	394°K	403°K	408°K
Control (no spike)	2.2 ± .3	5.9 ± .7	9.9 ± .0
Toluene-3,4-dithiol	3.4 ± .3	7.7 ± .9	12.8 ± 1.3
Dibenzothiophene	3.2 ± .4	7.5 ± .7	12.5 ± 1.6
Amylmercaptan	2.9 ± .2	7.2 ± .9	12.1 ± 1.0
p-Toluenethiol	2.7 ± .4	-	11.5 ± 1.2
Thiophenol	2.6 ± .6	6.6 ± .8	11.1 ± 1.4
1-Naphthalenethiol	2.4 ± .2	-	10.6 ± .9
n-Butyl sulfide	2.1 ± .1	5.3 ± .8	9.1 ± 1.1
n-Amyl sulfide	1.9 ± .4	4.9 ± .5	8.6 ± .9
n-Butyl disulfide	1.7 ± .2	4.8 ± .4	7.7 ± .8
n-Amyl disulfide	1.5 ± .1	4.1 ± .8	7.7 ± .4
i-Amyl disulfide	1.3 ± .3	3.8 ± .5	7.2 ± .7

Copper-Spiked Jet A

Various metals and metal salts are suspected of contributing to fuel instability (Ref. 18-20, 26, 53, 54). Copper is considered especially active. The introduction of copper metal foil into Jet A samples increases the amount of deposit (168 hours at 394°K). The amount of increase is related to the surface area of Cu introduced (Figure 26).

TABLE 18. EFFECT OF COPPER METAL ON JET A STABILITY (Deposit on 18mmx18mm coverslip after 168 hours at 394°K)

Cu Added (cm^2)	mg deposit
0	.110 ± .01
1.6	.186 ± .01
3.2	.233 ± .02
6.5	.246 ± .05

However, deposition does not occur on the copper surface but preferentially on the glass surfaces. The implication that the acceleration is due to dissolved copper compounds was tested by adding copper(II) acetylacetonate ($Cu(acac)_2$) to Jet A. This reagent dissolves readily in Jet A at concentrations up to 10 ppm Cu. The effects on deposition (168 hours, 394°K) are shown in Figure 27. The similarity of slope with that for the copper metal case is remarkable and perhaps fortuitous. Nonetheless, no evidence of heterogeneous catalysis by the metal surface is observed.

TABLE 19. EFFECT OF DISSOLVED COPPER ON JET A STABILITY (Deposit on 18mmx18mm coverslip after 168 hours at 394°K, copper added as copper (II) acetylacetonate)

Cu Added (ppm Cu)	mg deposit
0	.110 ± .01
.10	.119 ± .01
.20	.133 ± .03
.48	.225 ± .02
.90	.195 ± .01
4.9	.181 ± .01
7.5	.304 ± .01
9.9	.325 ± .01

Deposit Precursors

The HPLC method developed for monitoring tetralin hydroperoxide decomposition may provide a technique for the detection and separation of deposit precursors. Detection of the effects of aging on Jet A via HPLC analysis is shown in Figure 28. All four runs were conducted using .2M CH_3CN in 65/35 isooctane/chloroform as mobile phase at a flow rate of 2.0 ml/min. The upper trace is that of the refractometer and the lower that of the UV detector. The concentrations of polar constituents (retention volumes $>$ 6 ml) obviously increase as the sample is aged at 394°K. The areas of these peaks continue to increase throughout the 7 day aging period.

Quantitation of these polar constituent peaks as an alternative to the coverslip method for monitoring deposit formation was considered. The RI response to the major constituents (hydrocarbons) provides a convenient internal standard. When the simple sum of peak heights for the polar constituents divided by the height of the RI peak for hydrocarbons is used as the HPLC parameter, the relationship to deposit weight shown in Figure 29 results. A more sophisticated HPLC parameter might improve the correlation as might improvement of the chromatographic resolution. Precision and reproducibility have not been determined.

Another fuel property which was considered as an indicator of fuel degradation is dielectric constant. The fuel dielectric constant for Jet A increases as the fuel is aged. Unfortunately, the magnitude of the increase is not sufficiently large compared to the uncertainty in the measurement, by the method employed, to yield a viable method (Figure 30).

Synfuels

The nine synfuel samples were analyzed by the HPLC method described above. The resulting chromatograms (Figure 31-35) show marked differences in content of polar constituents. However, all the synfuels exhibit larger polar peaks than does Jet A (Figure 31). Aging of these samples for 168 hours at 394°K produced the deposit weights (on the coverslips) given in Table 20. The results bear an interesting relationship to the HPLC

TABLE 20. DEPOSITION FROM SYNFUELS
(mg deposit on coverslip after 168 hours at 394°K)

Sample (Ref. 54)	Deposit weight
Jet A	0.061
33315	0.505
33317	0.231
33341	2.390
33342	3.914
33365	-
33368	0.218
33409	2.646
33411	2.330
33516	2.957

analyses of the synfuels prior to aging. The samples producing low deposit weights (33315, 33317, 33368) are those having the largest peaks corresponding to polar constituents. Highest deposit weights occurred in fuels with the smallest polar constituent peaks. The sample 33516, the only coal-derived material studied, is anomalous in this regard. As in the case of Jet A, the size of these peaks does increase during aging as shown in Figure 36. A limited supply of the synfuels precluded further study of this interesting situation.

The deposit weights in Table 20 yield no correlation with sulfur, existing gum, nitrogen, or aromatic content (Ref. 54) of the synfuels (Figures 37 and 38). In each case, the point for the coal-derived fuel (33516) is distinguished as an open circle.

Deposit Characterization

Deposits produced in the accelerated storage testing of Jet A are brown to black solids which adhere tenaciously to glass surfaces. While partially soluble in solvents such as THF and CH_2Cl_2, the deposits were not completely dissolved by any solvents tested. This insolubility renders spectral analysis difficult. Thermal deposits are even more intractable. Deposits from accelerated storage of the model fuel first appear as viscous liquids. With continued aging, solids develop which are very similar in appearance to the storage deposits from Jet A. These model system deposits are more soluble in THF and CH_2Cl_2 than are the Jet A deposits.

Elemental analysis of the model deposits produces results very similar to those for Jet A. The addition of nitrogen heterocycles does not significantly alter nitrogen content of the deposit (Table 21). However, analysis of model deposit produced by passing air through the model fuel at 423°K (302°F)

TABLE 21. ELEMENTAL ANALYSES OF MODEL DEPOSITS
(Nitrogen compounds added at 10 ppm N level)

Fuel Sample	% C	% H	% N
Model	70.20	6.13	.29
Model + pyridine	71.95	6.43	.27
Model + quinoline	73.41	6.30	.28
Model + indole	73.08	6.30	.31

contains much higher nitrogen concentrations (2.7% N). The origin of such large amounts of nitrogen in the deposits has not been explained. The purification methods applied to the dodecane and tetralin render the presence of nitrogen-containing impurities highly unlikely. The validity of the analytical results was confirmed by independent analyses in another laboratory. That nitrogen from air or the sample container should be incorporated into deposits seems equally implausible.

Conventional transmission infrared (IR) spectral analysis on thin films of deposit (Figure 39) yields spectra of poor resolution. The multiple-internal-reflectance IR method produces spectra of improved resolution (Figures 40 and 41) which facilitates band assignment. Strong OH and carbonyl stretching bands appear in spectra of both model and Jet A deposits. A weak peak in the region for peroxide stretching, 900-850 cm^{-1} (Ref. 96), is also observed. Minor changes are observed in deposits from Jet A spiked with nitrogen compounds (Table 22) but the general similarity is remarkable.

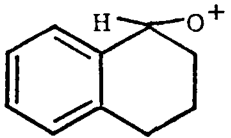
Gel permeation chromatography was performed on a THF solution of Jet A storage deposit (dissolution of the sample was not complete). The columns used have exclusion limits of 400 and 1000. Retention volume for a 1000MW standard for this system is 18.2 ml. The chromatogram (Figure 42) thus indicates very little material of MW < 1000.

TABLE 22. MAJOR INFRARED ABSORPTION PEAKS IN FUEL DEPOSITS
(wavenumbers in cm^{-1}, sh=shoulder, d=doublet, b=broad, Jet A spiked at 5 ppm N)

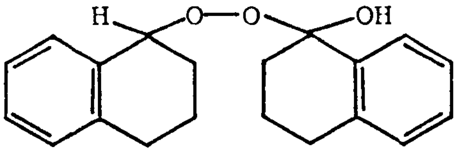
Model Deposit	Jet A Deposits		
	Control	Pyridine	Indole
3300	3400	3400	3400
3062	3050		
2958	2960	2950	2963
2937(sh)	2930	2920	
2875	2860(d)	2863	2865(d)
1765	1762(sh)	1760(sh)	1768
1722	1720	1722	1712
1713	1711	1707	
1666	1665		1640
1595	1594	1600	
1573			
1458(d)	1450	1444	1445
1385			
1185(d)	1179	1180	1183
1125(d)	1125	1120	1134
1052	1050(b)		1054
1028			
907	905(sh)		
872	885	845	892
750(b)	750		

The application of secondary ion mass spectrometry (SIMS) to structural elucidation of organic solids has only recently begun to receive much attention (Ref. 97). The spectrum for the Jet A storage deposit (Figure 43) shows no peaks above m/e=113. Coupled with the GPC result, this finding is surprising. Major peaks at 23 and 39 may be assigned to Na^+ and K^+ from the glass plate on which the deposit was formed.

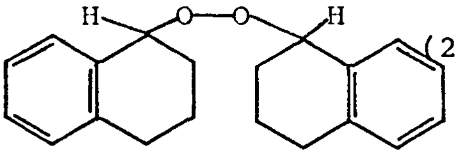
The SIMS spectrum for the model deposit (Figure 44) appears considerably more complex with peaks over the entire range to above m/e=450. The principal peak at 73 could be assigned to C_4H_9O, perhaps a fragment from an oxidized dodecane derivative or from fragmentation and rearrangement of an oxidized tetralin species. Assignment of the 147 peak to



provides some support for tetralin hydroperoxide/tetralone condensation. Small peaks are found at 310 and 294 suggestive of the two condensation products:

(310) 

and



(294)

However, the peroxide bond would be expected to lead to facile cleavage. The peak at 15 indicating methyl fragment ions suggests involvement of dodecane derivatives.

The SIMS spectrum of Jet A thermal deposit changed rapidly when initially scanned. The initial spectrum (Figure 45) contains an intense peak at 73 (compare to the model deposit, Figure 44). However, after approximately ten minutes in the spectrometer, the spectrum changed to that in Figure 46. No further change was then observed in eight hours. A very thin surface layer of one material covering a thicker layer of a second is indicated. The sample was washed with hexane and air-dried prior to the analysis. Therefore, a surface coating of fuel was not the cause. That thermal deposits result from further reaction, on the heated metal surface, of compounds produced by reactions responsible for storage deposits is consistent with this observation. Peaks at 63 and 65 suggest the presence of copper; that at 56, iron; that at 23, sodium; and that at 39, potassium. Origin of the latter two is unclear.

CONCLUSIONS

The formation of deposits in Jet A and Diesel fuels at temperatures between 382 and 406°K in the presence of air is the result of condensation reactions involving polar precursors. These reactions are catalyzed by bases present in the liquid phase. Acceleration of deposition by bases is significant at concentration of the bases as low as 10^{-4}M (1 ppm N). The effectiveness of bases in promoting deposition is proportional to base strength within classes of compounds (pyridines, indoles, etc.) with the effectiveness of the classes decreasing in the order pyridines > quinolines >> indoles > pyrroles. The transition states appear to be entropy-controlled. Removal of polar fuel components via silica treatment not only increases stability but also destroys the catalytic effect of nitrogen bases. The bases, therefore, catalyze condensation reactions of polar fuel components but don't significantly accelerate the formation of these deposit precursors.

Thiols and dibenzothiophene destabilize Jet A while sulfides and disulfides inhibit deposition. None of the sulfur compounds produced an induction period for deposition. Apparently, therefore, the inhibition is not due to reduction of autoxidation products by the sulfur compounds. The considerable difference in temperature dependence of the influence of sulfur and nitrogen compounds suggests that different mechanisms operate in the two cases. Clearly, the effect of nitrogen compounds is related to their basicity. While the sulfur compounds are Lewis bases, sufficient data to test similar correlations with basicity are not available. That the effect is not due to radical initiation (via thermal cleavage of weak bonds to sulfur) by the sulfur compounds is indicated by the results of ABIN and benzoyl peroxide additions.

Both copper metal and soluble copper salts increase deposition rates. The lack of deposition on the copper metal surface and the similarity of surface area and concentration effects indicate solution phase phenomena in each case. If radical pathways are disregarded, coordination of oxygenated intermediates is the most likely role for copper ion.

Tetralin/dodecane provides an excellent system for modeling fuel stability. Despite the simplicity of this model "fuel", similarity to Jet A, a very complex system, is amazing. Composition, spectra, and appearance of deposits differ little. Catalytic effects of nitrogen heterocycles on deposition rates are parallel in the two cases. The rate of tetralin autoxidation is not affected by quinoline while the rate of tetralin hydroperoxide decomposition (producing tetralone and tetralol) is accelerated. Addition of tetralone increases deposition while addition of tetralol suppresses deposit formation. Addition of tetralin hydroperoxide and tetralone creates a much higher deposition rate which is further increased by addition of quinoline. Therefore, the rate-determining process in model deposit formation involves the ketone, hydroperoxide, and base catalyst.

Spectral evidence of -OH, -C=O, and -O-O- functional groups was found in both model and Jet A deposits. These data, elemental analyses, and secondary ion mass spectrometry results are consistent with the presence of tetralin hydroperoxide/tetralone condensation products in the model deposits. Lewis bases catalyze both the formation of tetralone via hydroperoxide decomposition as well as the subsequent condensation reactions.

Concentrations of polar components of Jet A increase continually in heated fuel exposed to air. HPLC analysis of these constituents demonstrates a correlation with deposition. Stabilization of Jet A and Diesel by silica treatment corresponds to removal of the polar constituents from the fuel. The HPLC method may afford a convenient stability testing method.

The influence of individual Lewis bases on stability is a function of basicity, structural, and steric effects. Similar variations occur with sulfur compounds. Hence no simple correlation between stability and bulk nitrogen or sulfur concentration should be expected. Indeed, none was found for the synfuels tested. Possible correlation with content of polar oxygenated species should be investigated further.

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FIGURE 1. Rate of Gum Formation in Jet A

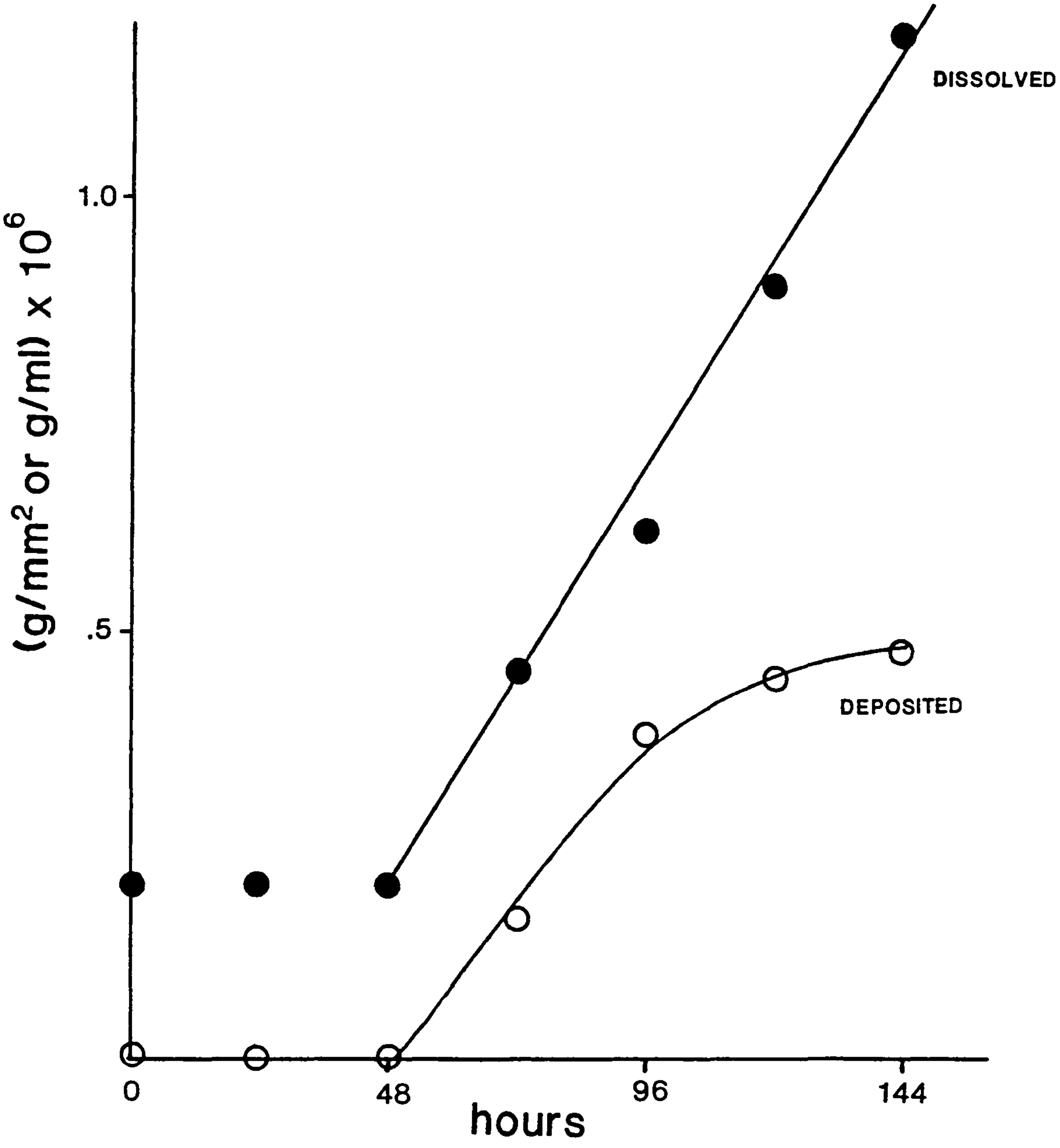


FIGURE 2. Effect of Extract on Dissolved Gum

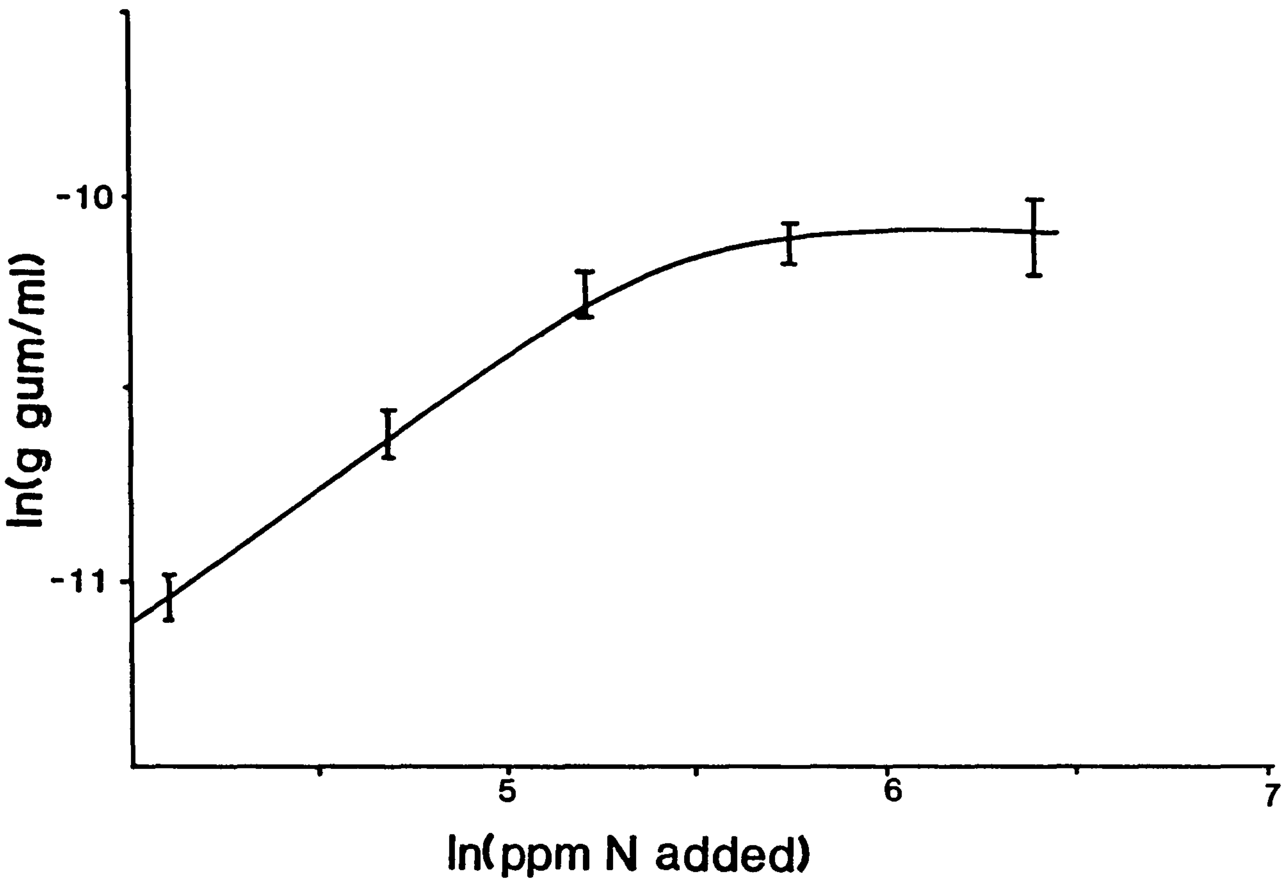


FIGURE 3. Effect of Extract on Deposited Gum

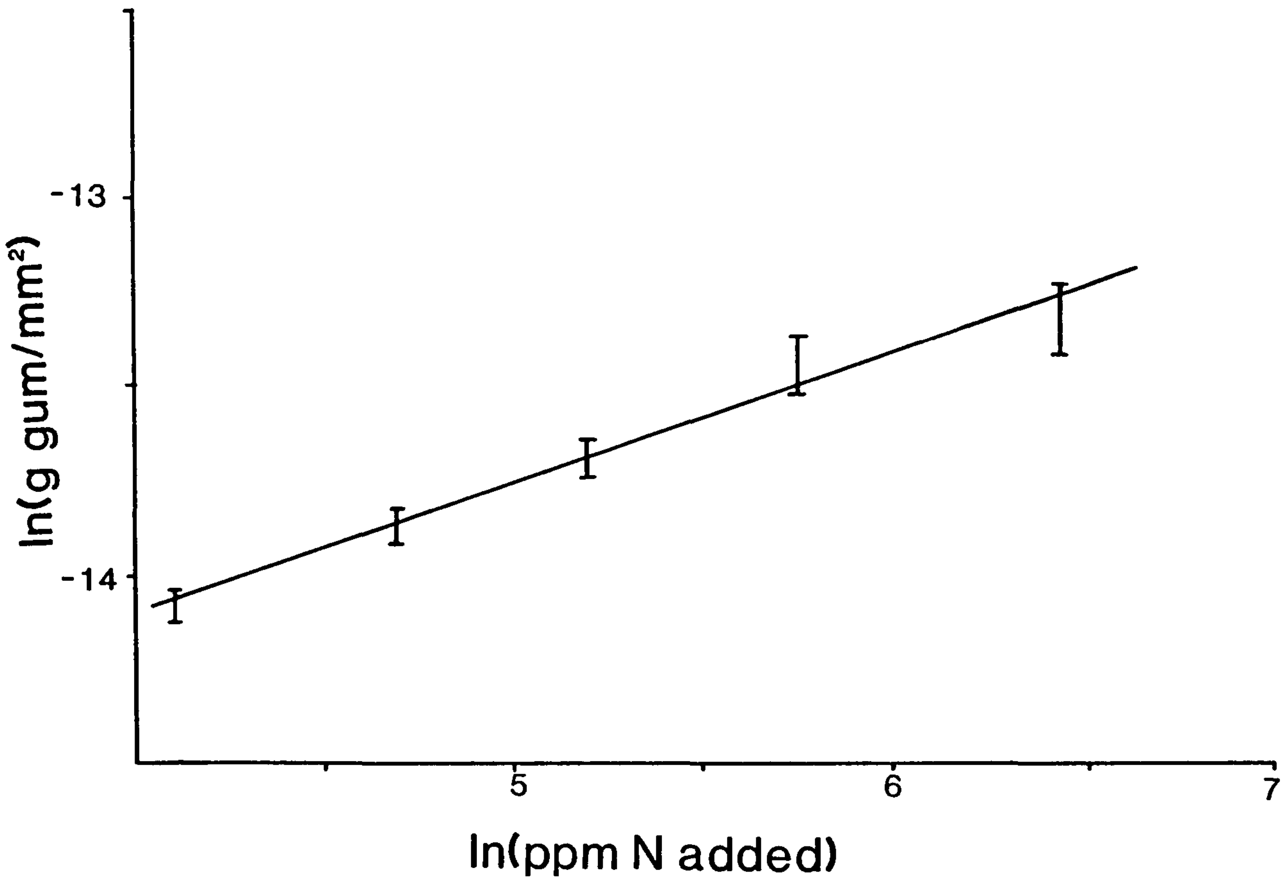


FIGURE 4
Effect of Added Nitrogen Concentration on Deposition Rate

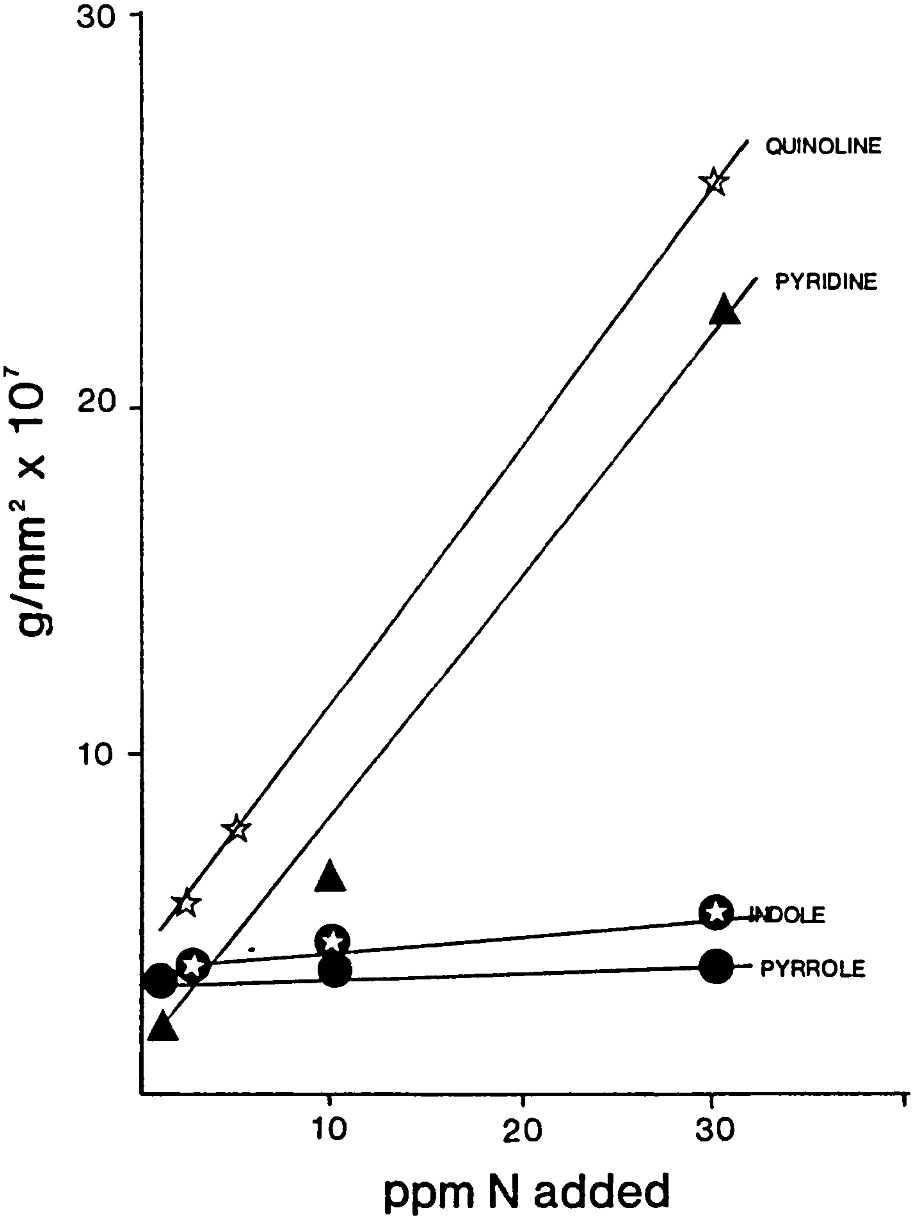


FIGURE 5
Jet A - Deposition Rate and Basicity

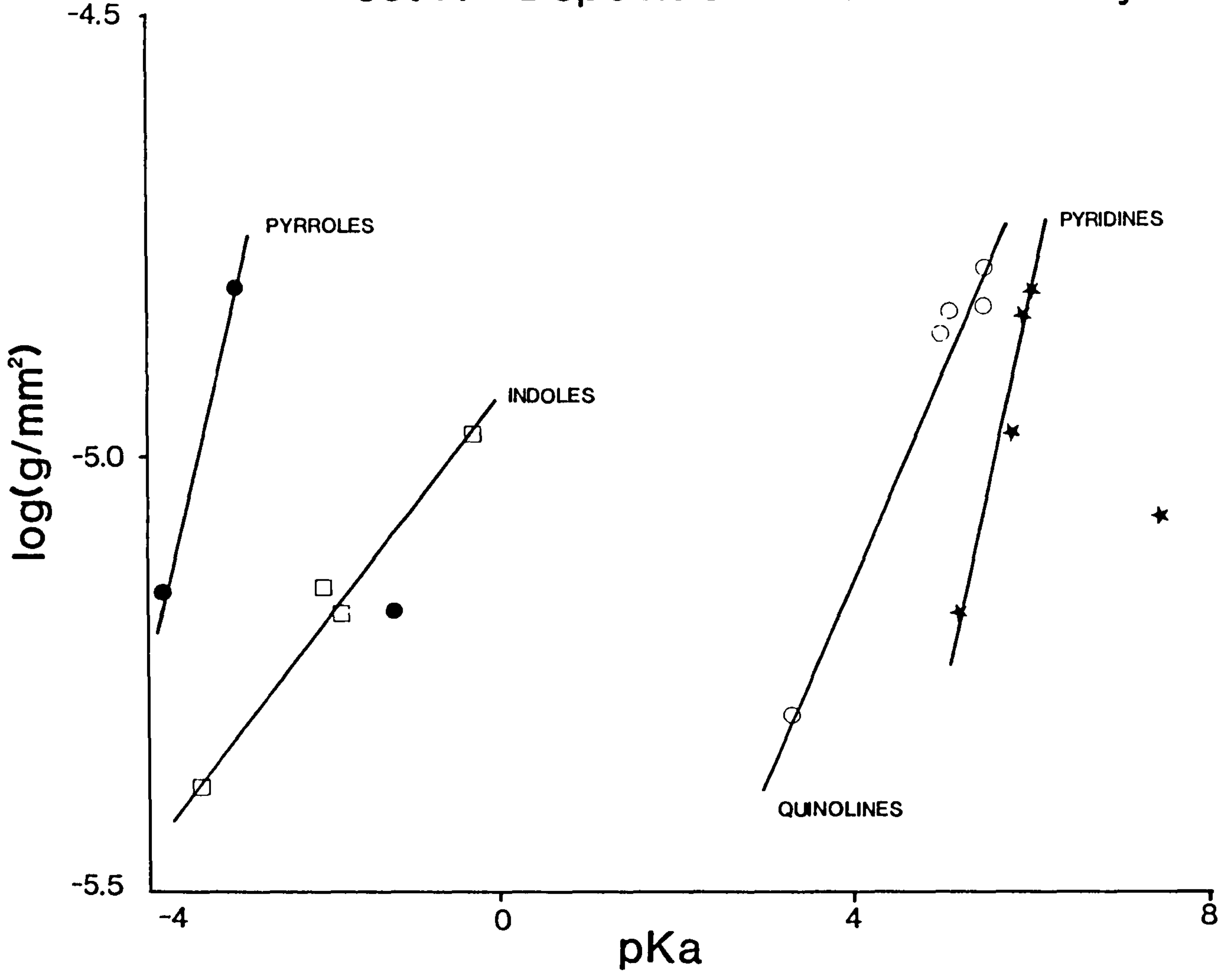


FIGURE 6
Temperature Dependence of Deposition Rate

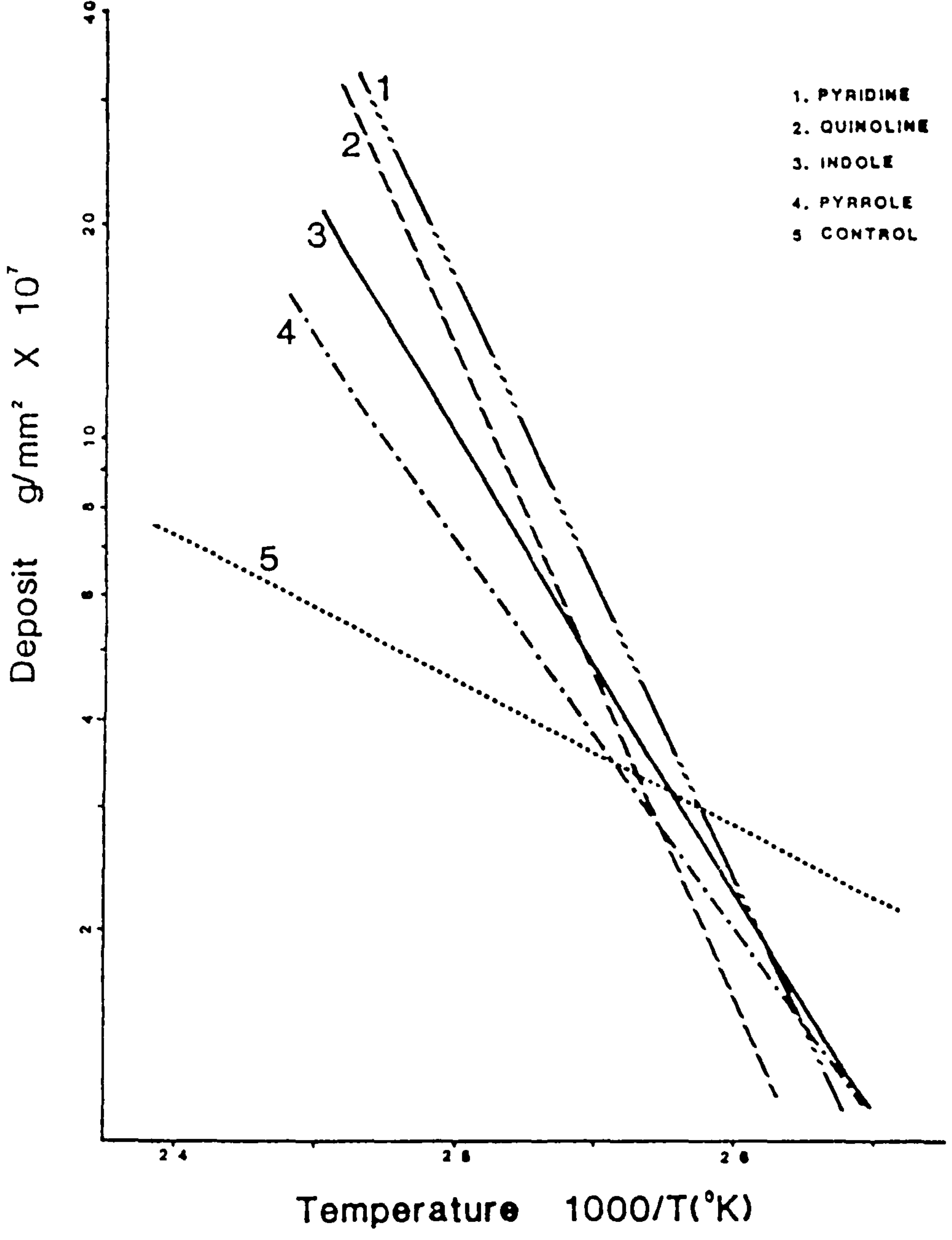


FIGURE 7

Arrhenius Slope/Intercept Relationship

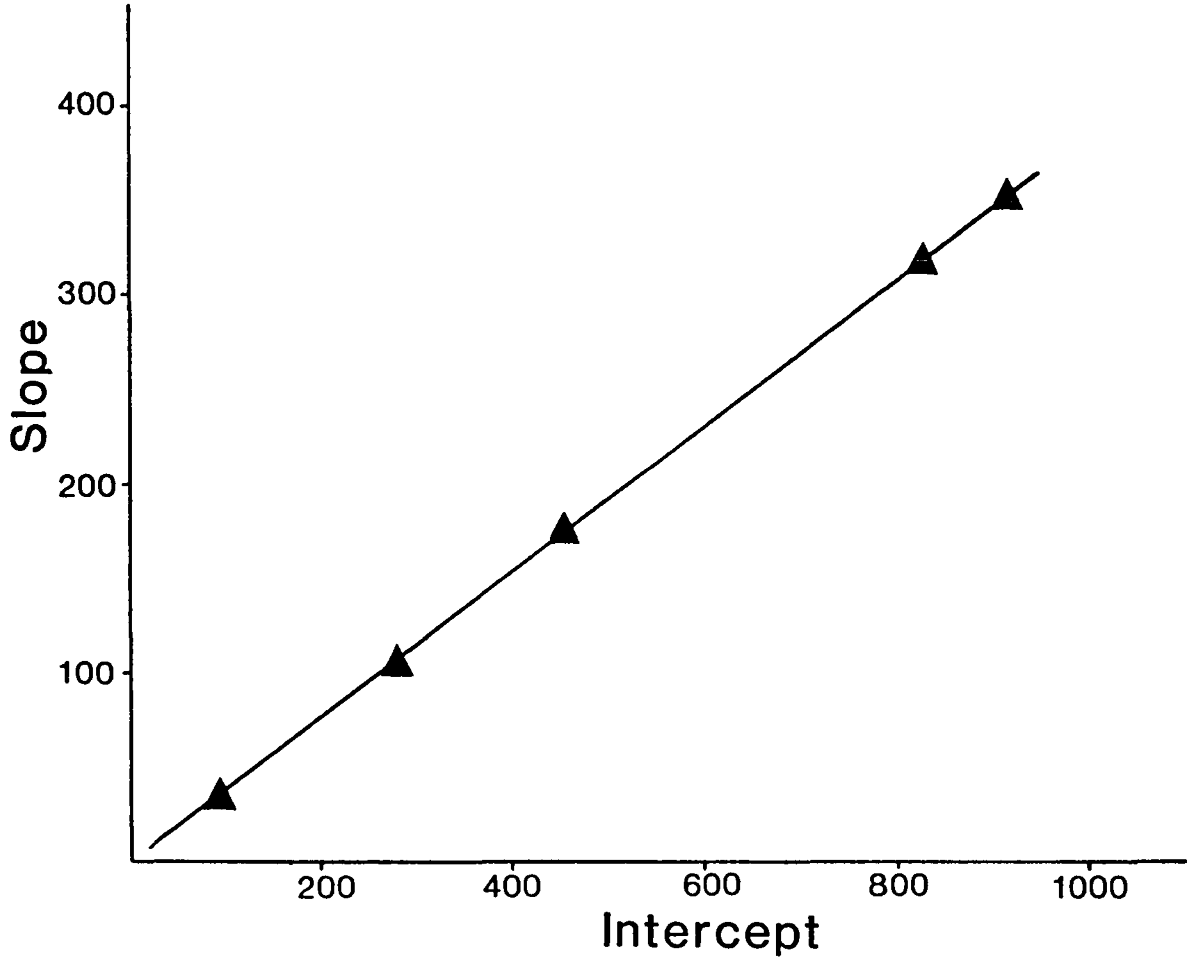


FIGURE 8. Transformed Slope/Intercept Relationship

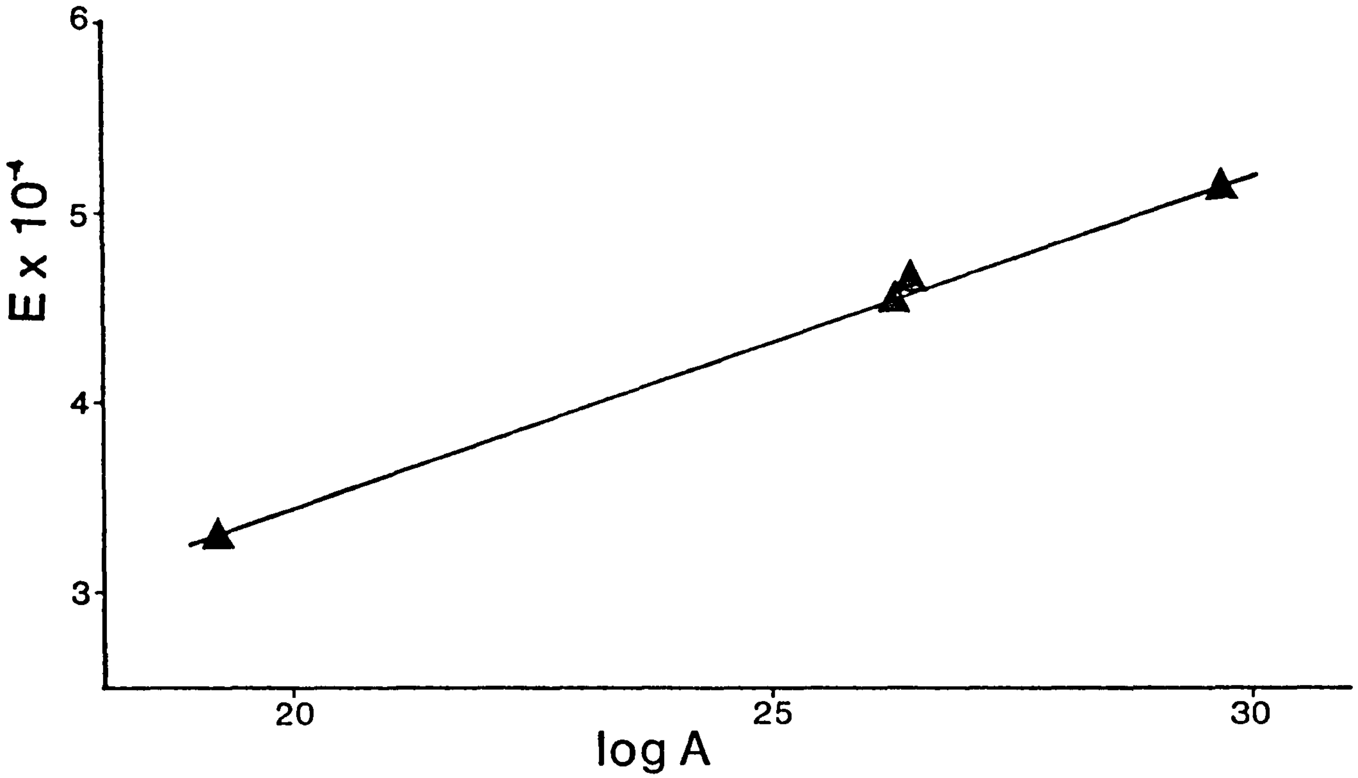


FIGURE 9

PNMR Spectrum of Jet A

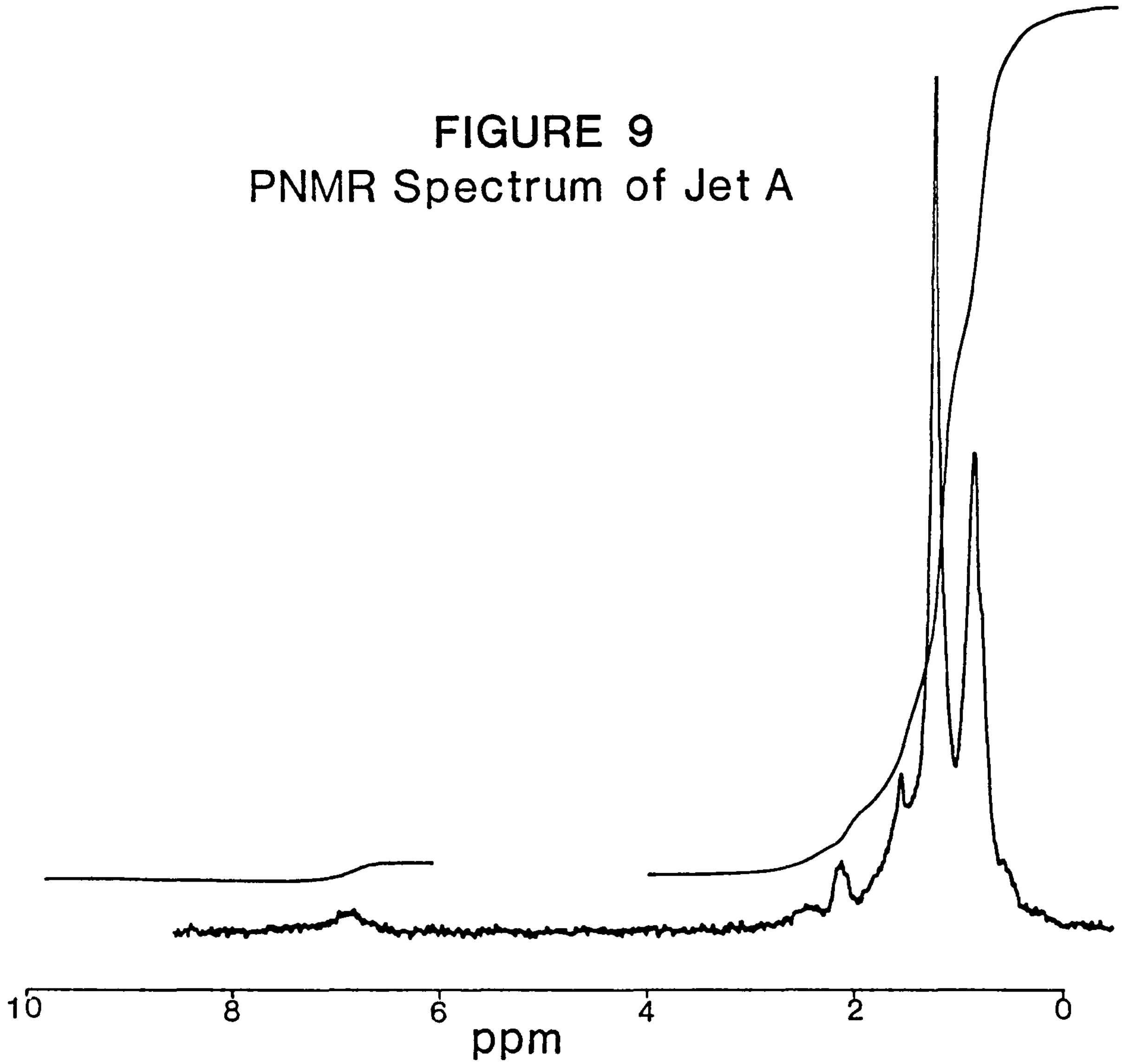


FIGURE 10.
PNMR Spectrum of Diesel

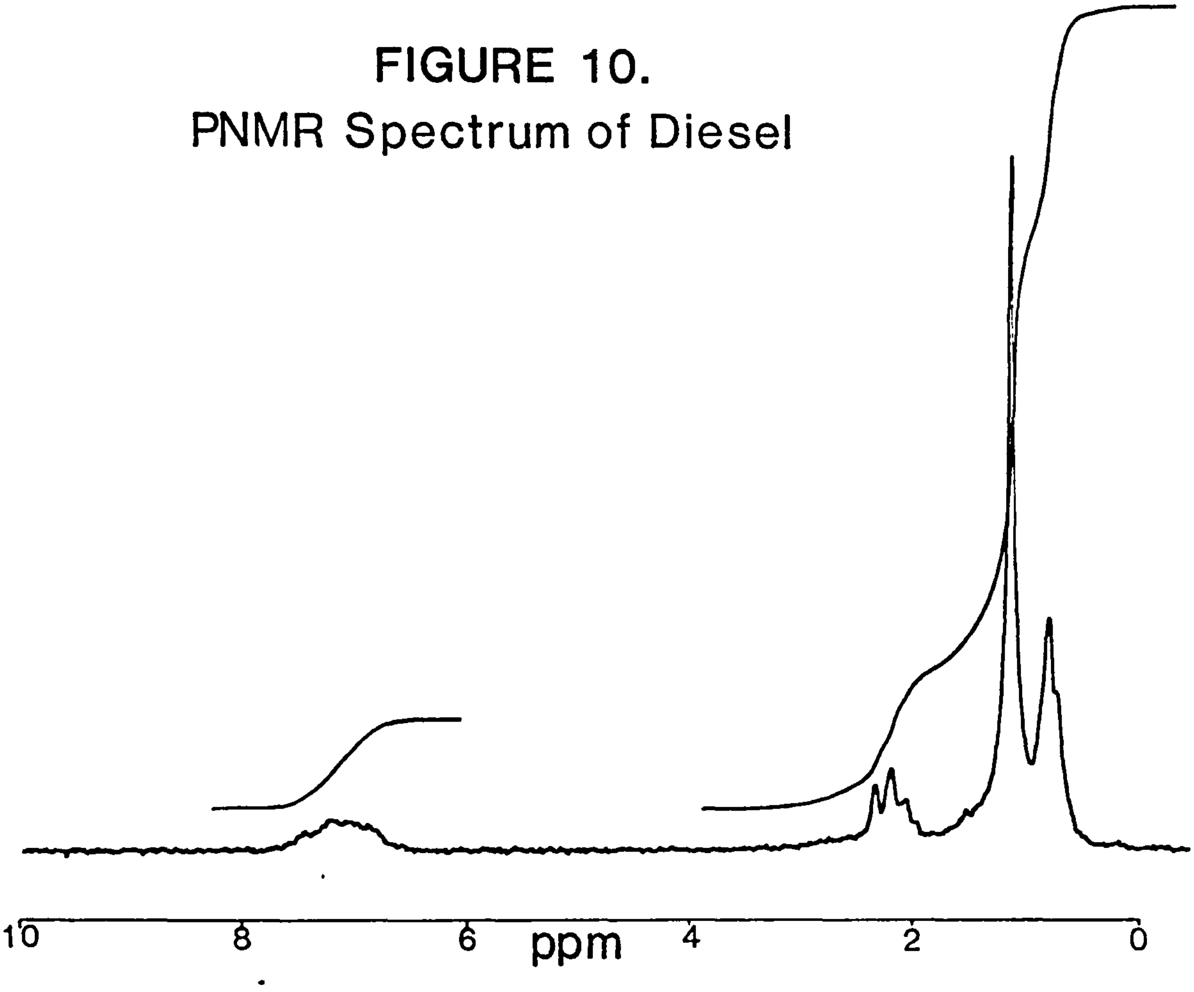


FIGURE 11

Diesel - Deposition Rate and Basicity

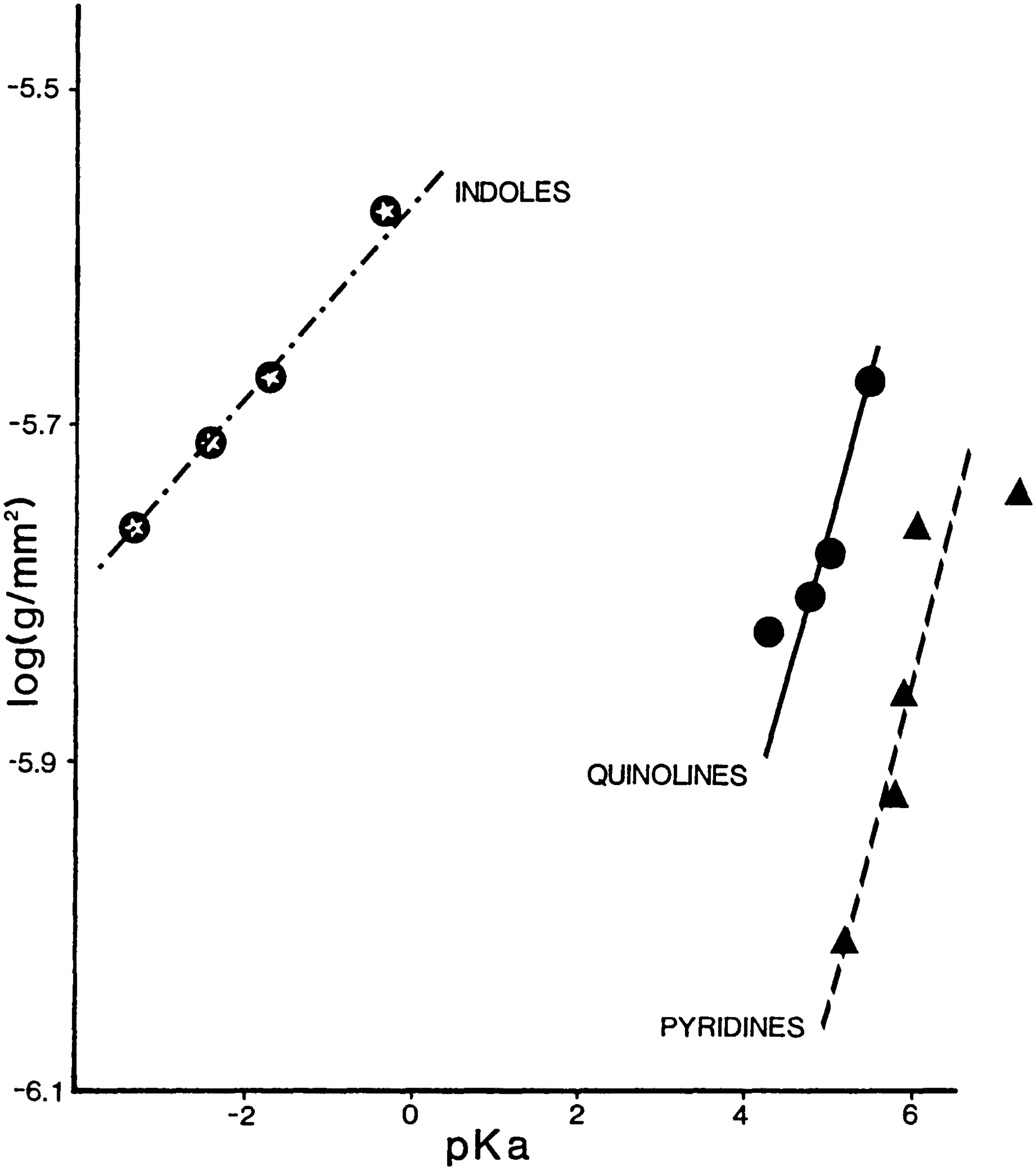


FIGURE 12

Comparison of Nitrogen Compound Effects in Jet A and Diesel Fuels

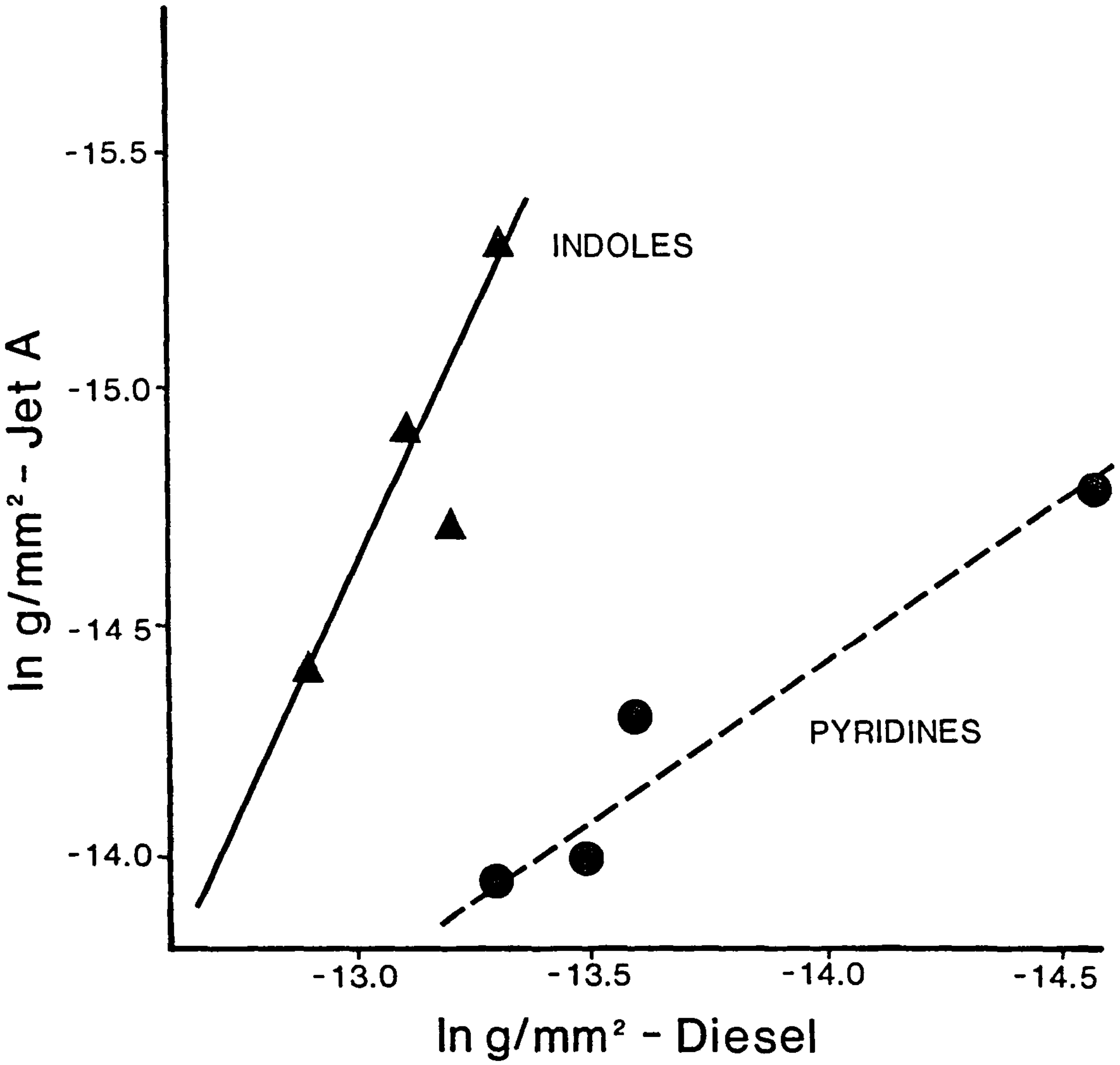


FIGURE 13. Deposit-forming Activity of Various Fractions of Diesel Fuel

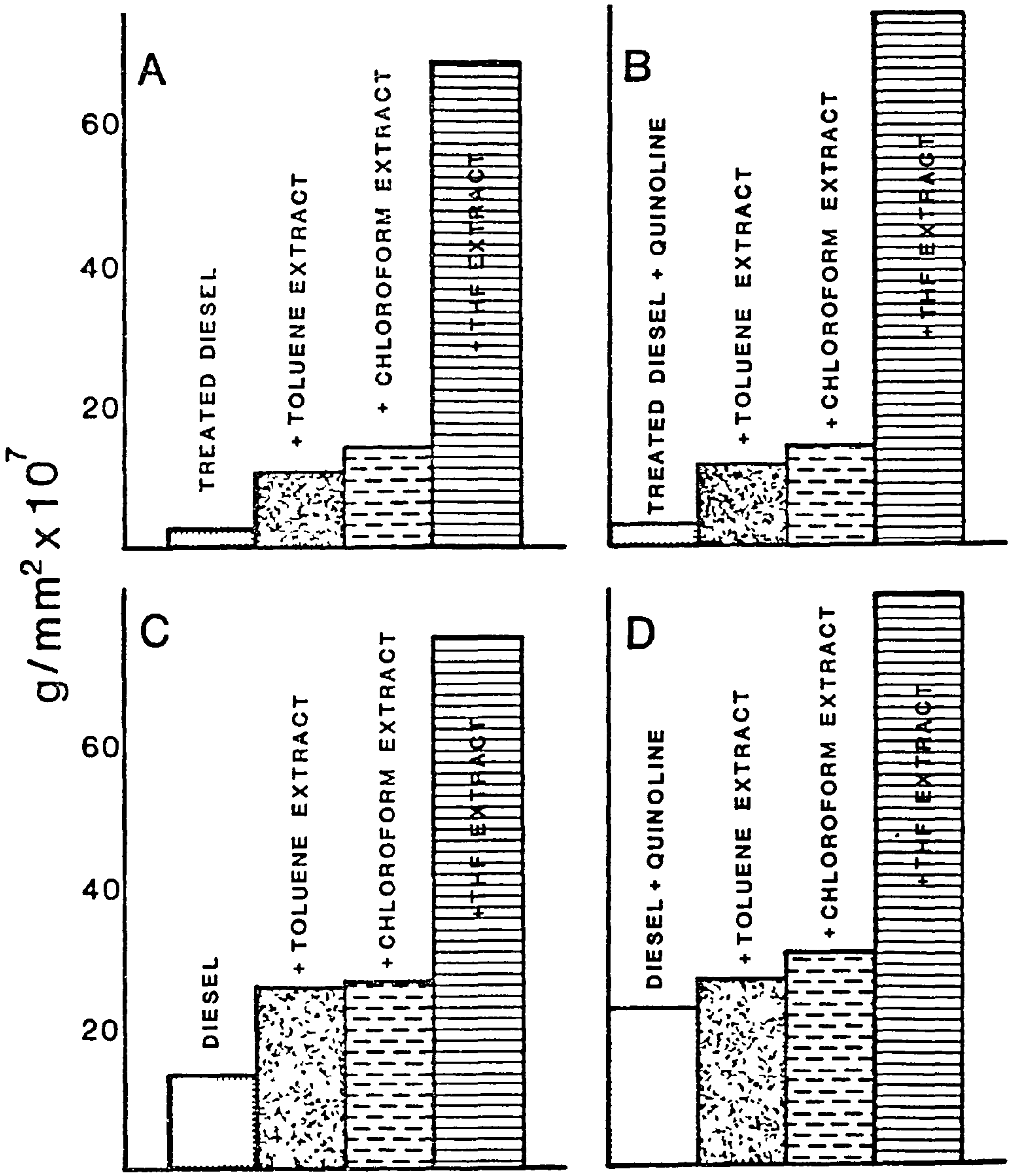


FIGURE 14

Effect of Silica Treatment on Jet A. Analysis by HPLC

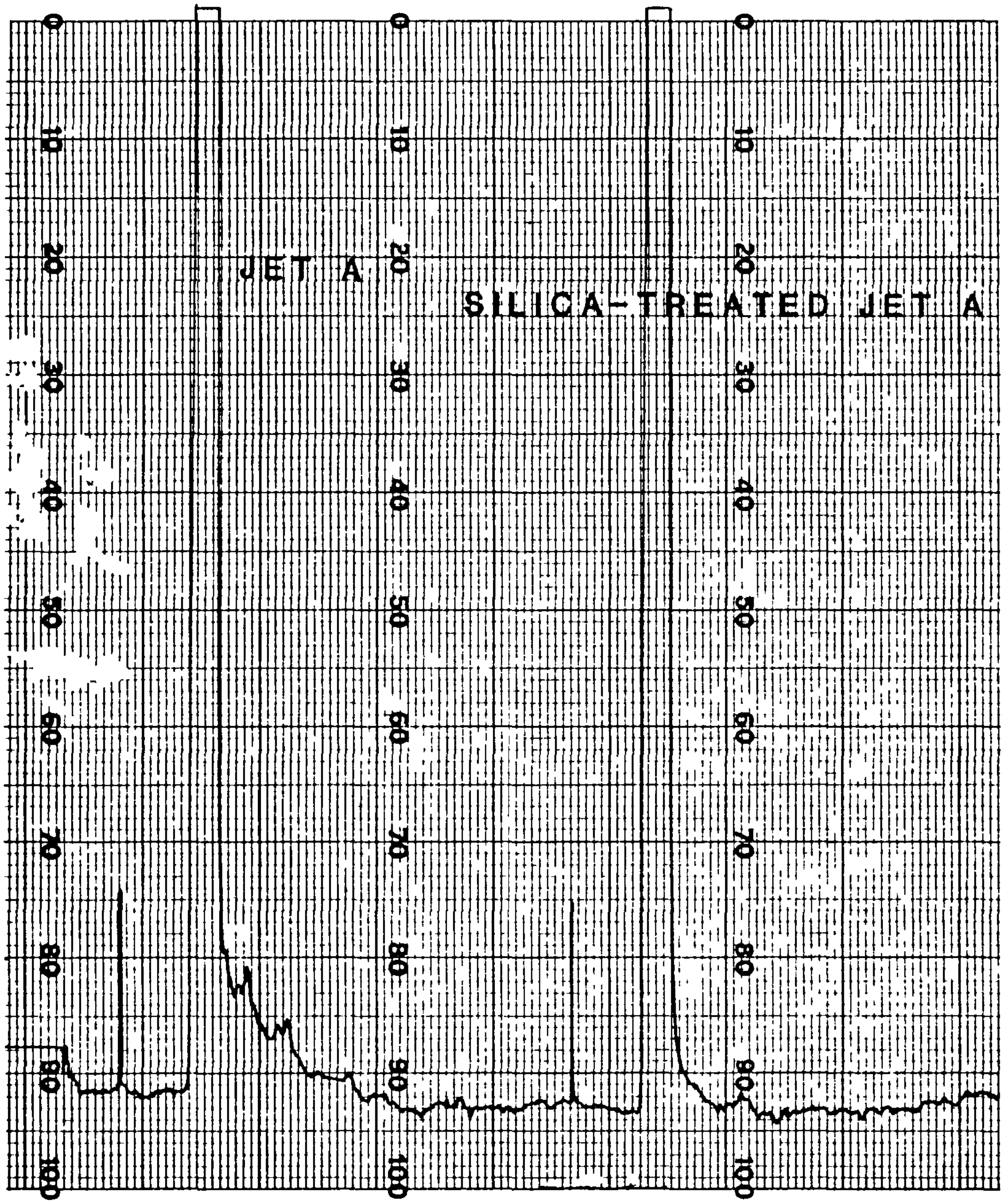


FIGURE 15

Effect of Silica Treatment on Diesel. Analysis by HPLC

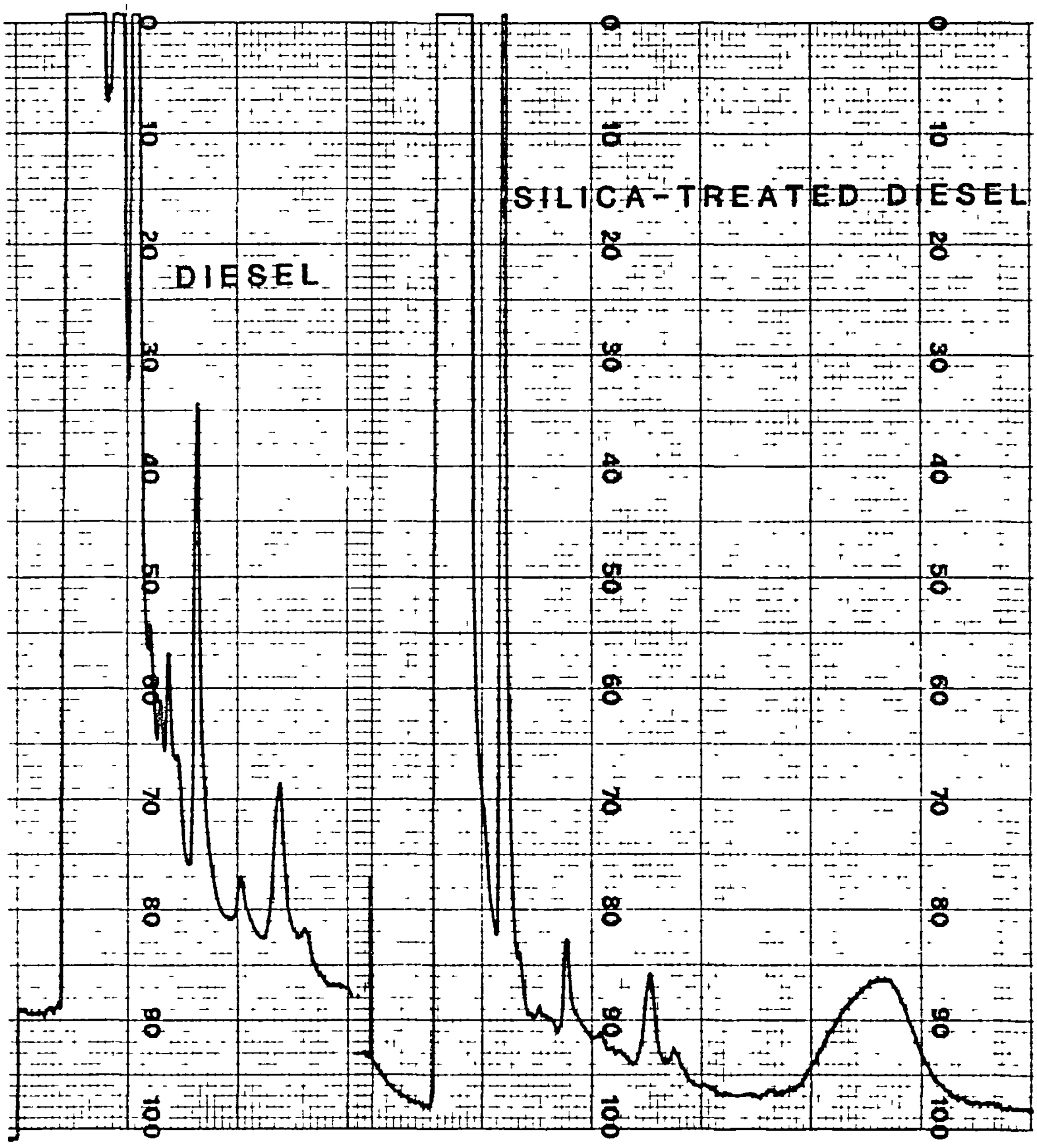


FIGURE 16
Rate of Tetralin Oxidation

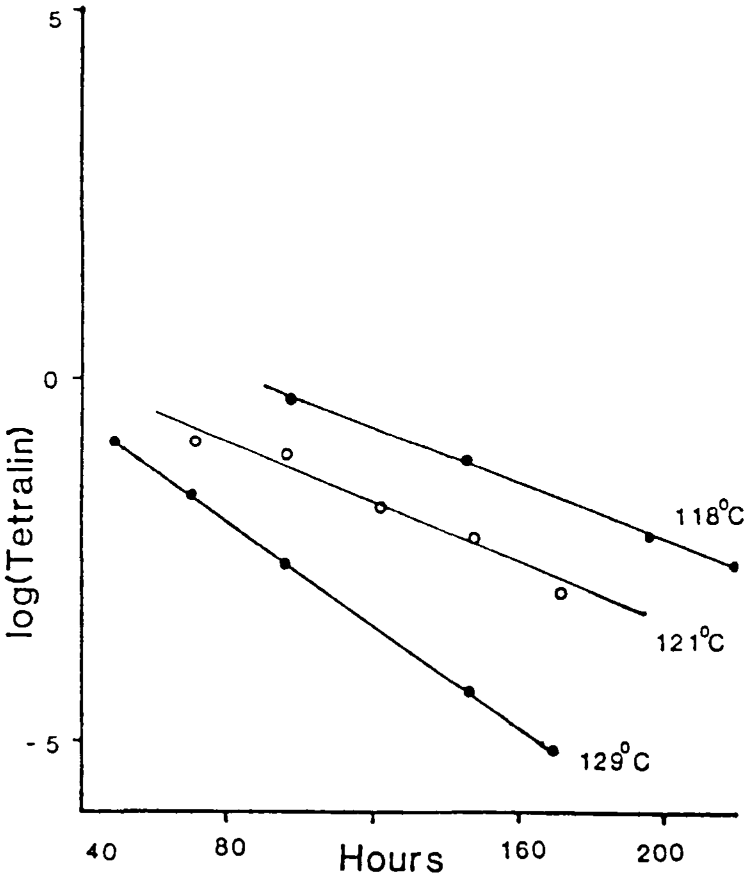


FIGURE 17
Effect of Nitrogen Heterocycles on Deposit Formation in the Model System

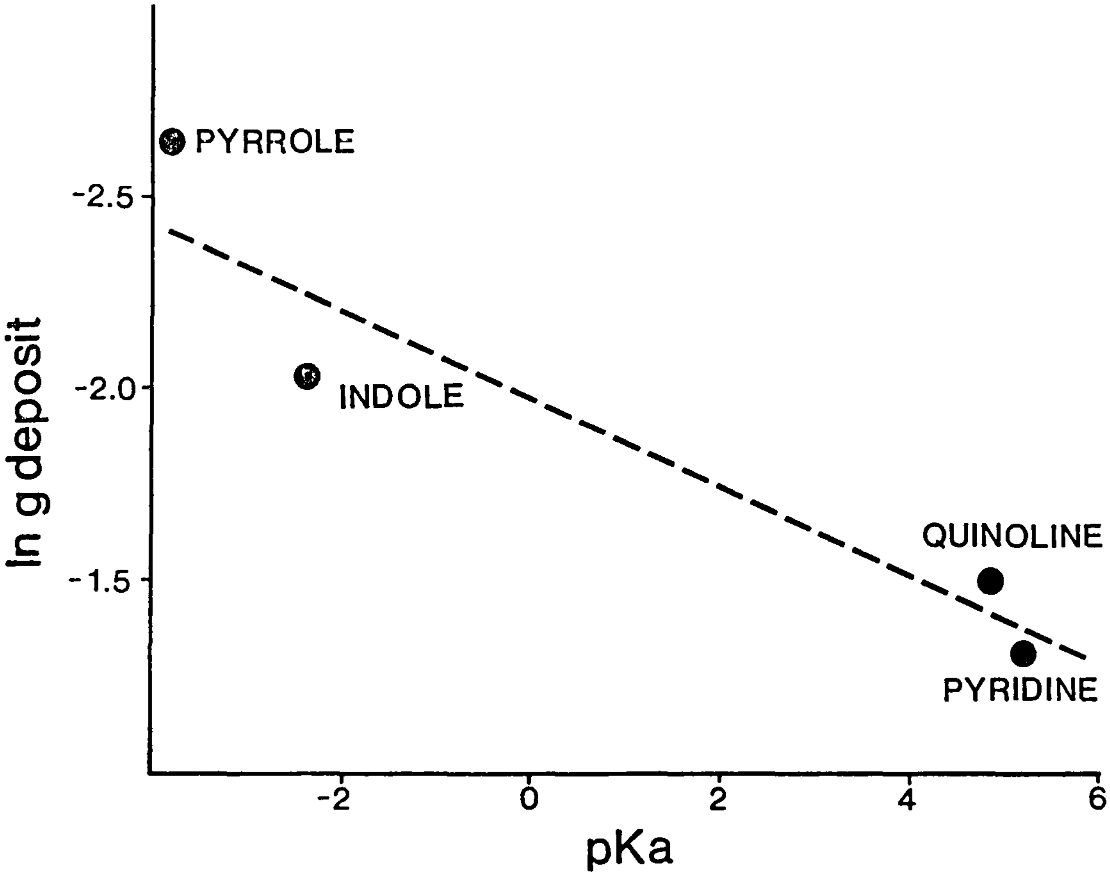


FIGURE 18

Effect of Quinoline on Tetralin Autoxidation

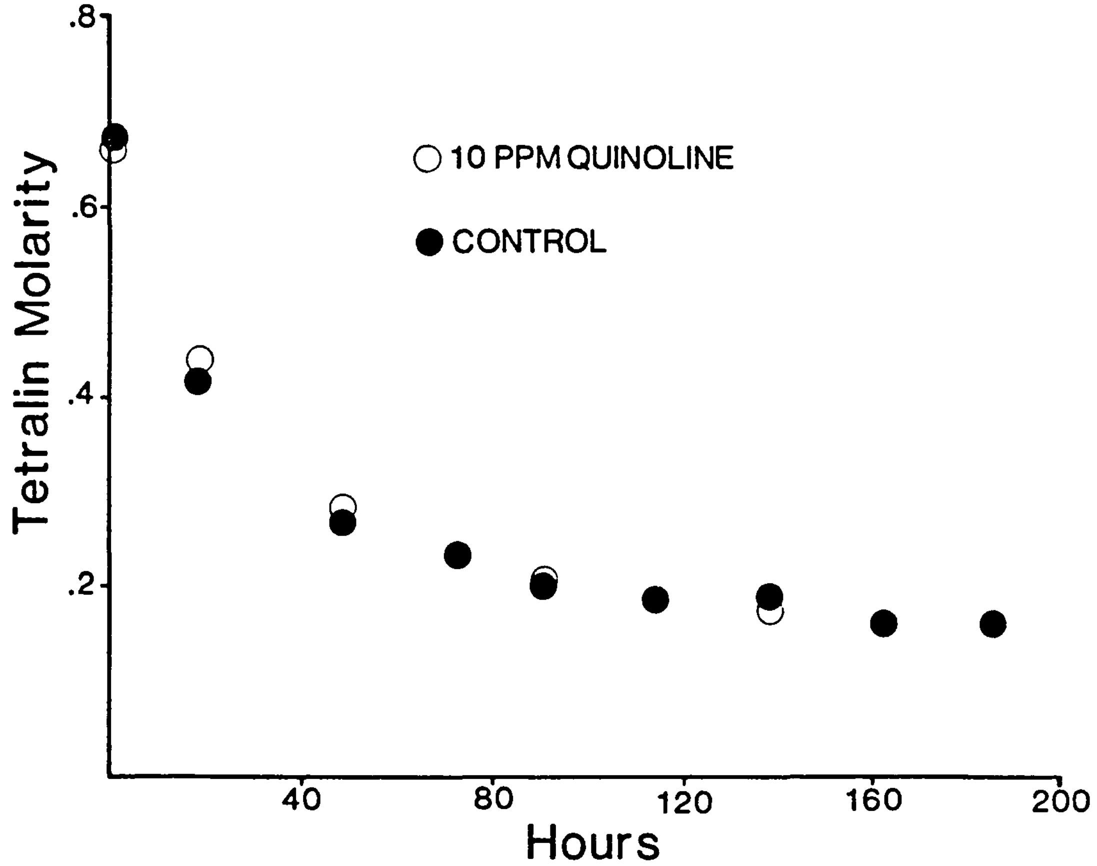


FIGURE 19

Effect of Mobile Phase Composition on HPLC Retention Time

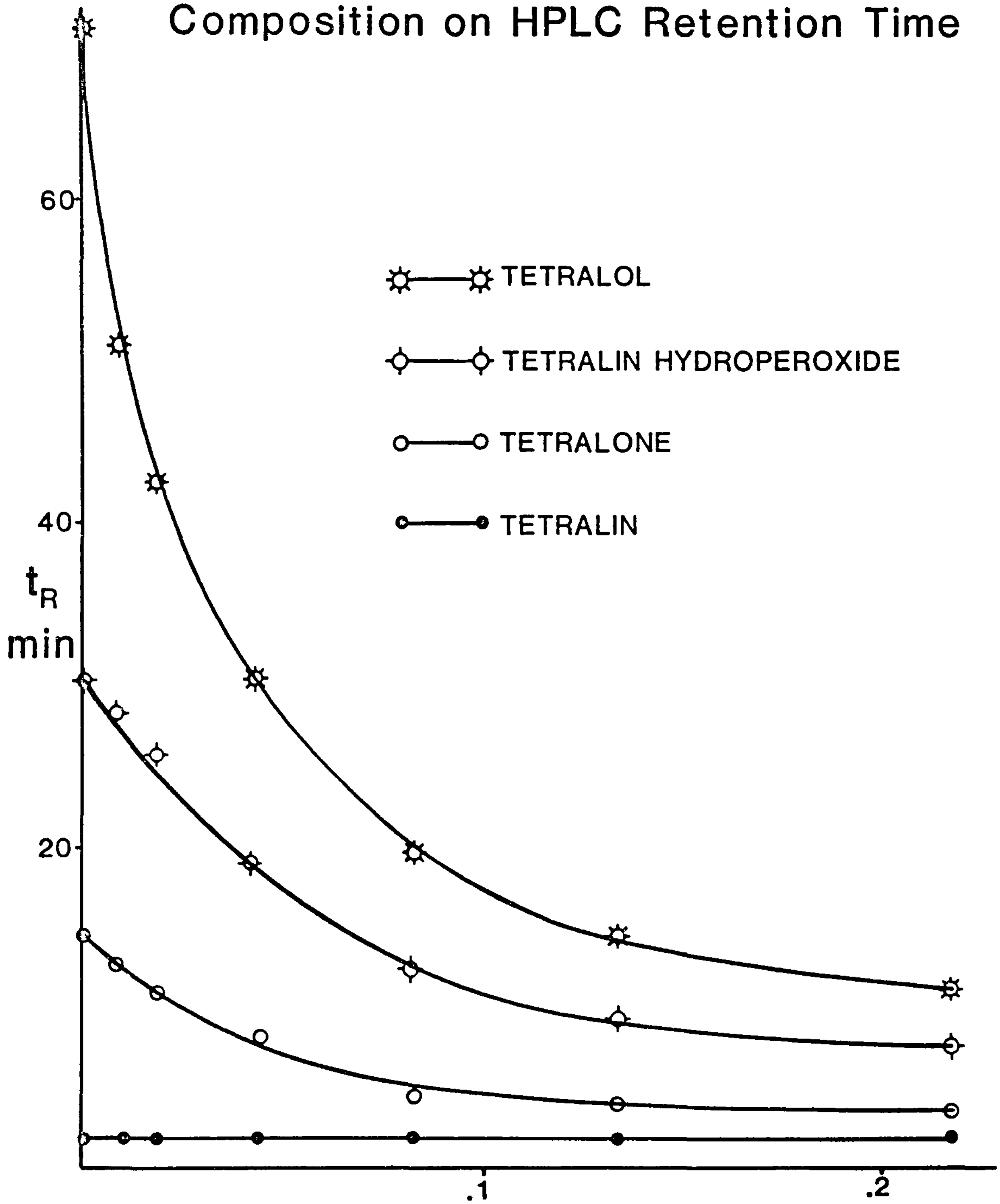


FIGURE 20. Model System HPLC CHROMATOGRAM

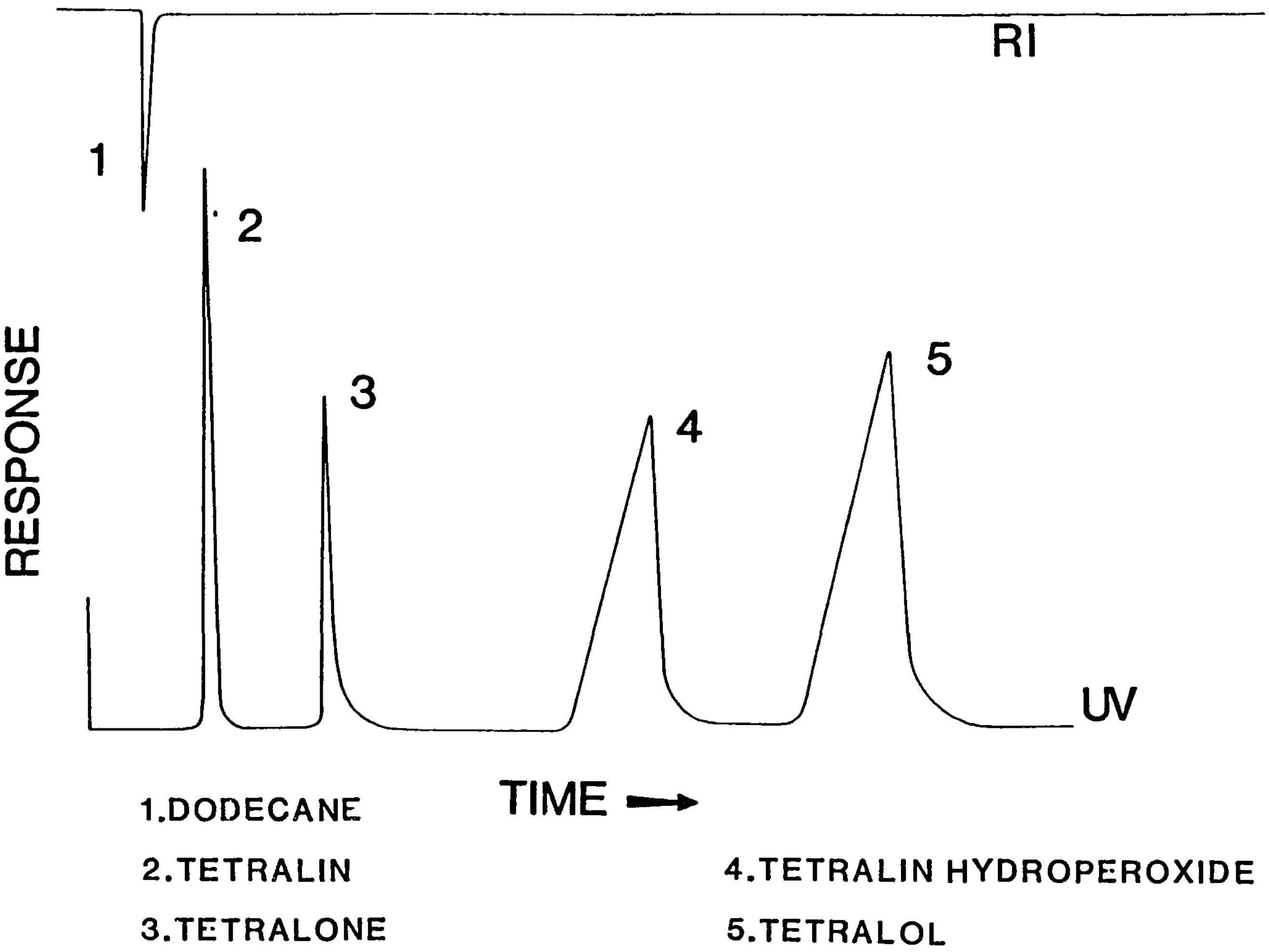


FIGURE 21

Effect of Nitrogen Heterocycles on Tetralin Hydroperoxide Decomposition

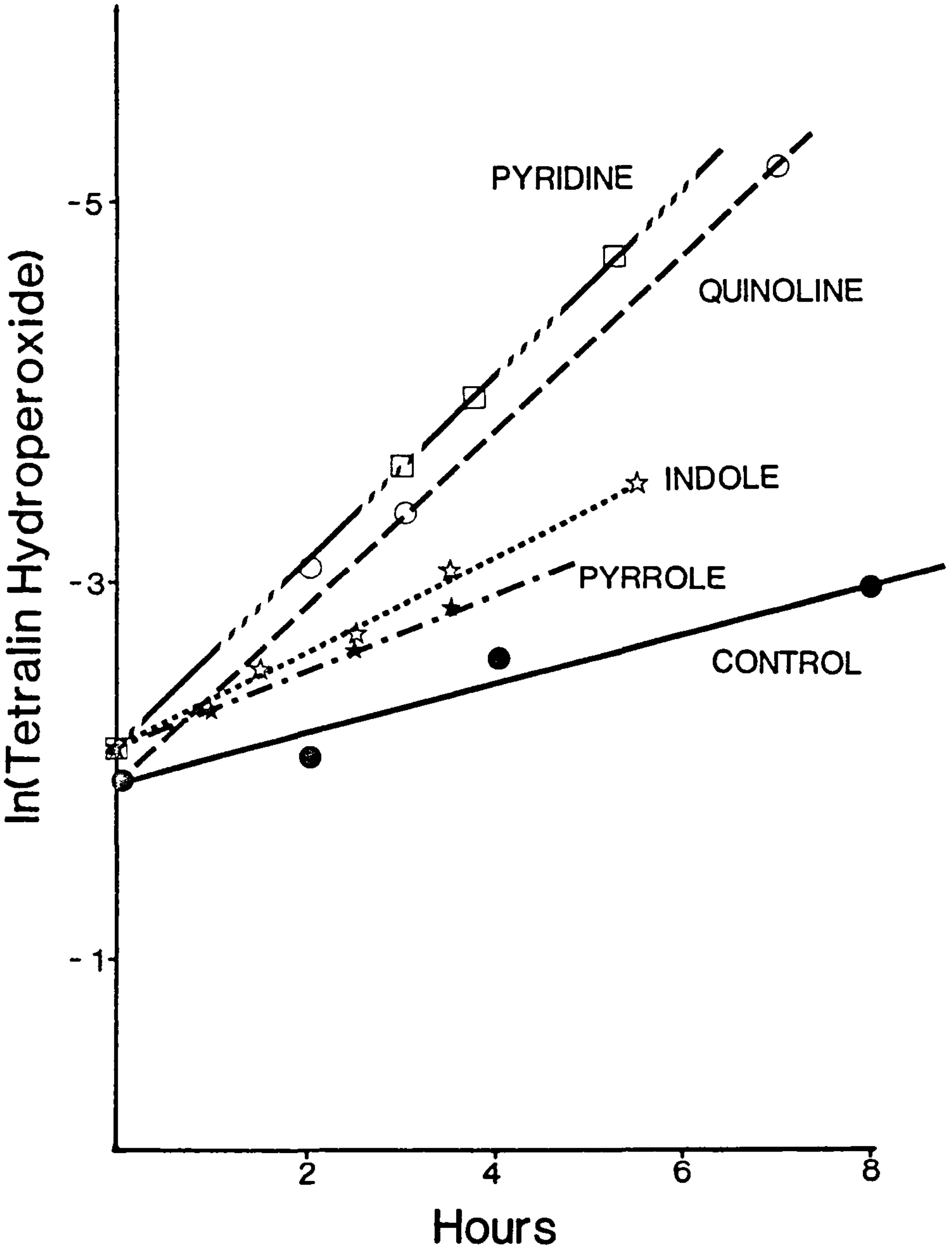


FIGURE 22

Effect of Oxygen-Containing Compounds upon Deposit Formation

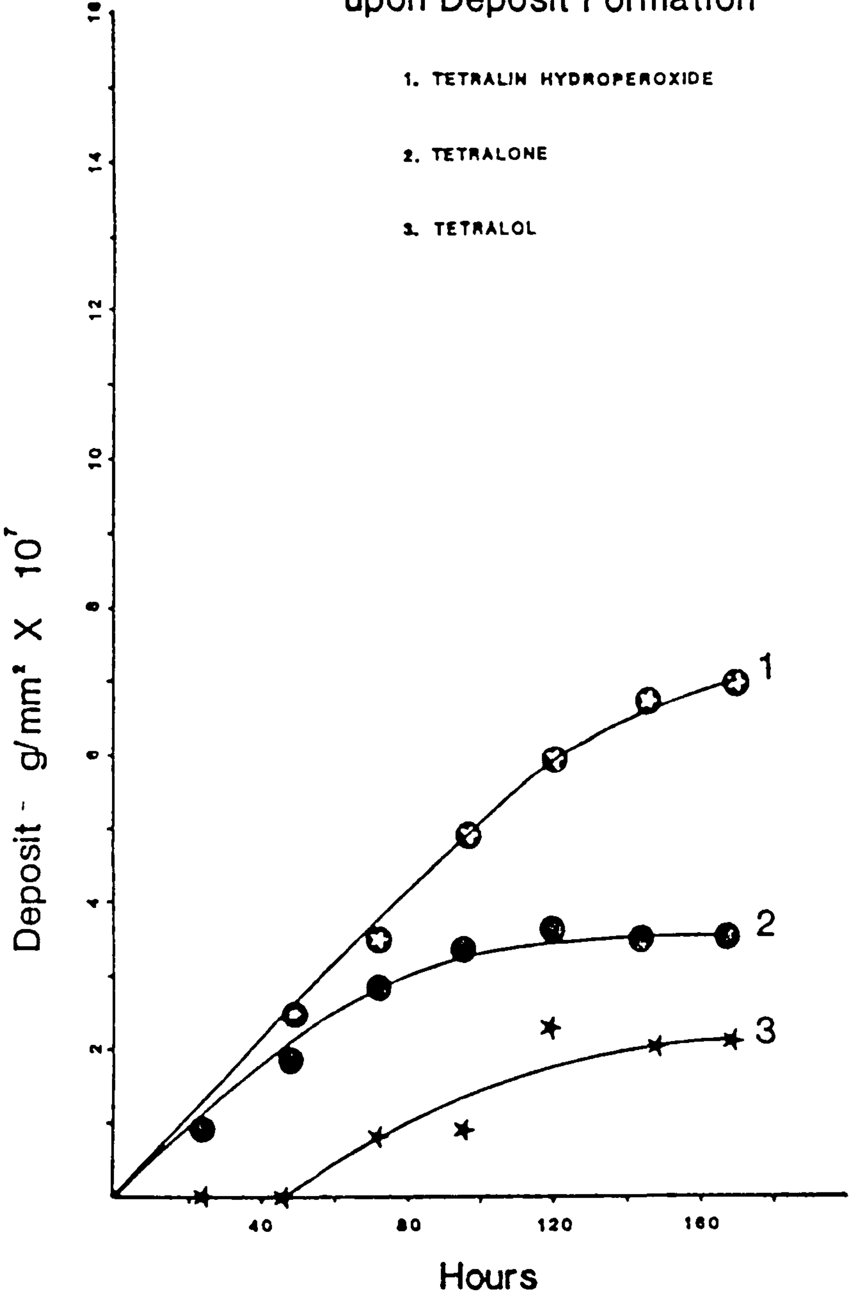


FIGURE 23

Combined Effect of Oxygen-Containing Compounds upon Deposit Formation

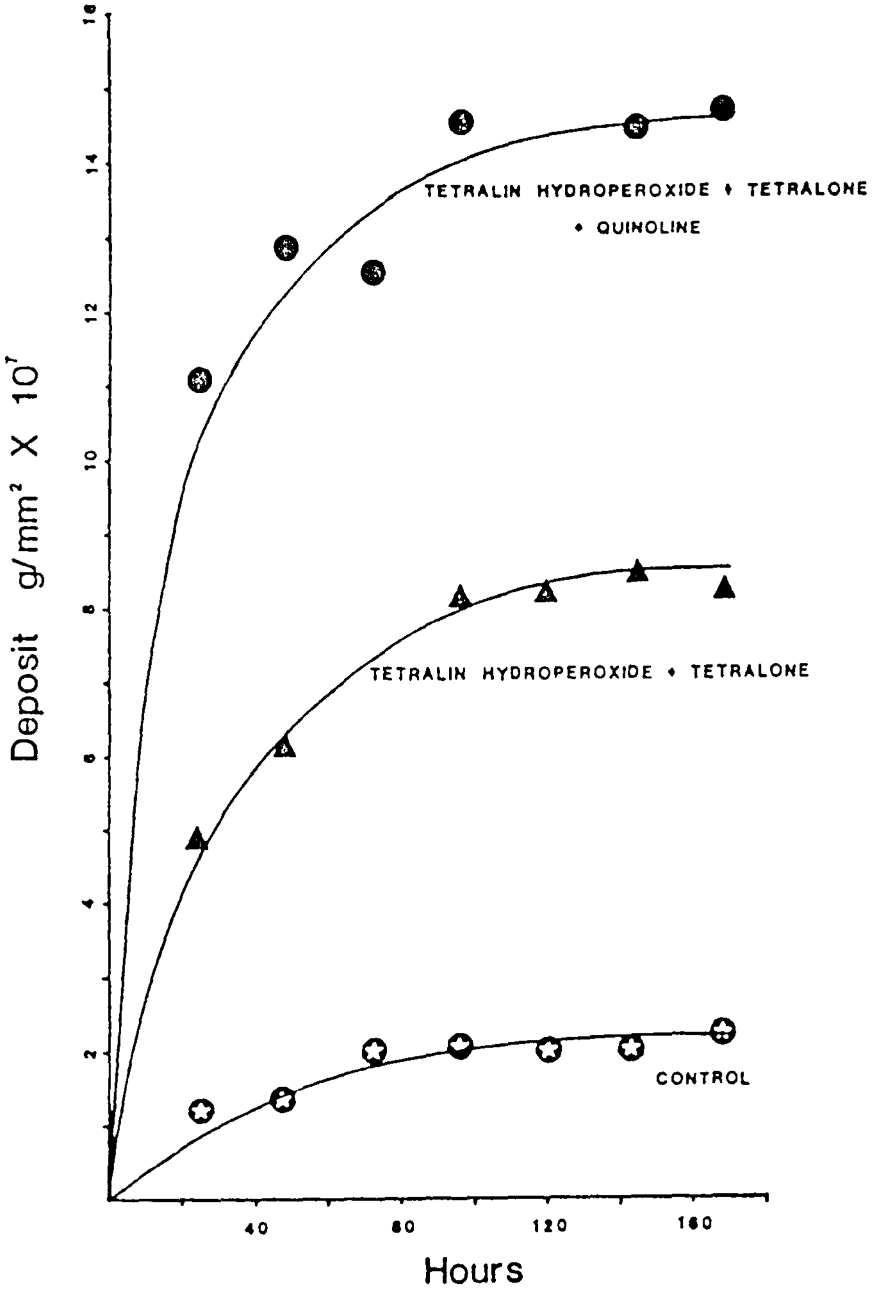
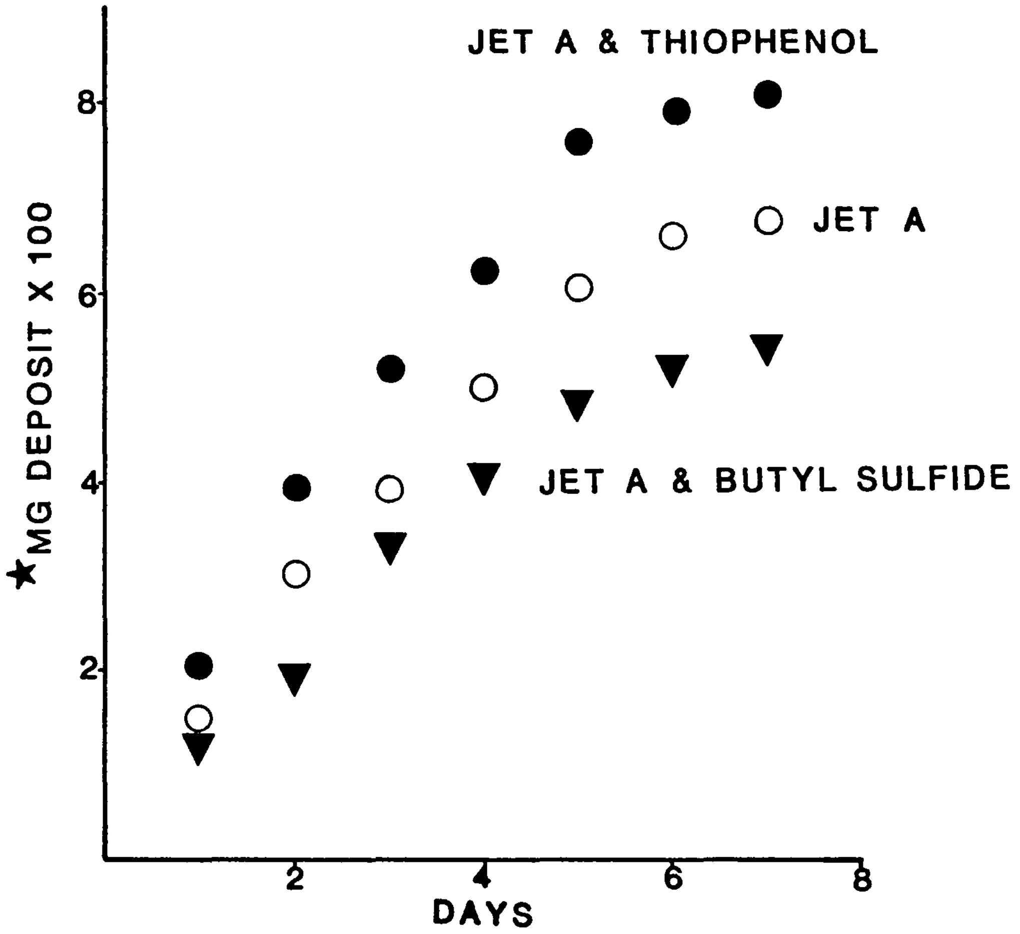


FIGURE 24
The Effect of Sulfur Compounds on Deposition Rate



★ON 3.24 CM^2 COVERSLIP

FIGURE 25
Temperature Dependence of Sulfur Compound Effects

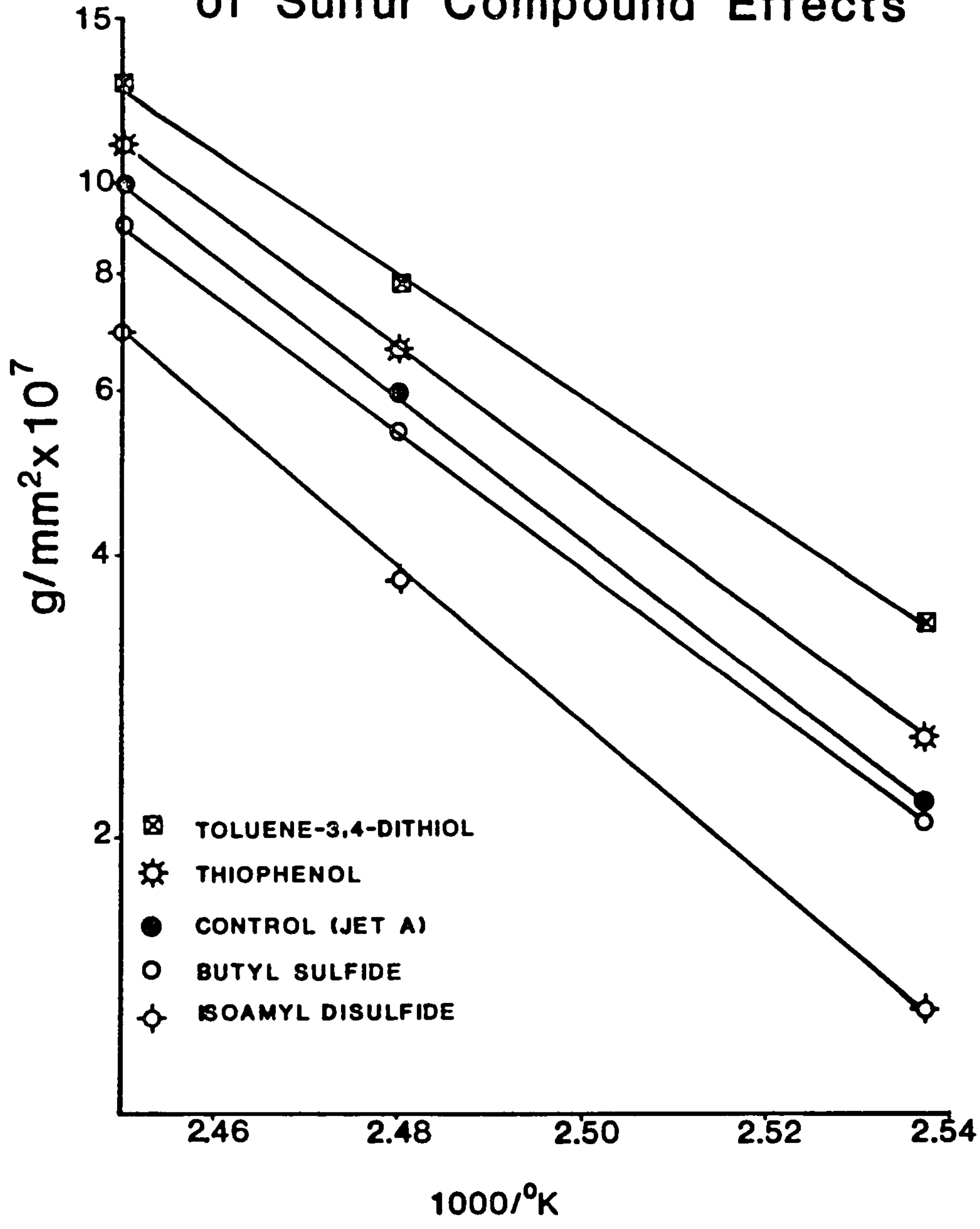


FIGURE 26
Effect of Cu Metal on Jet A

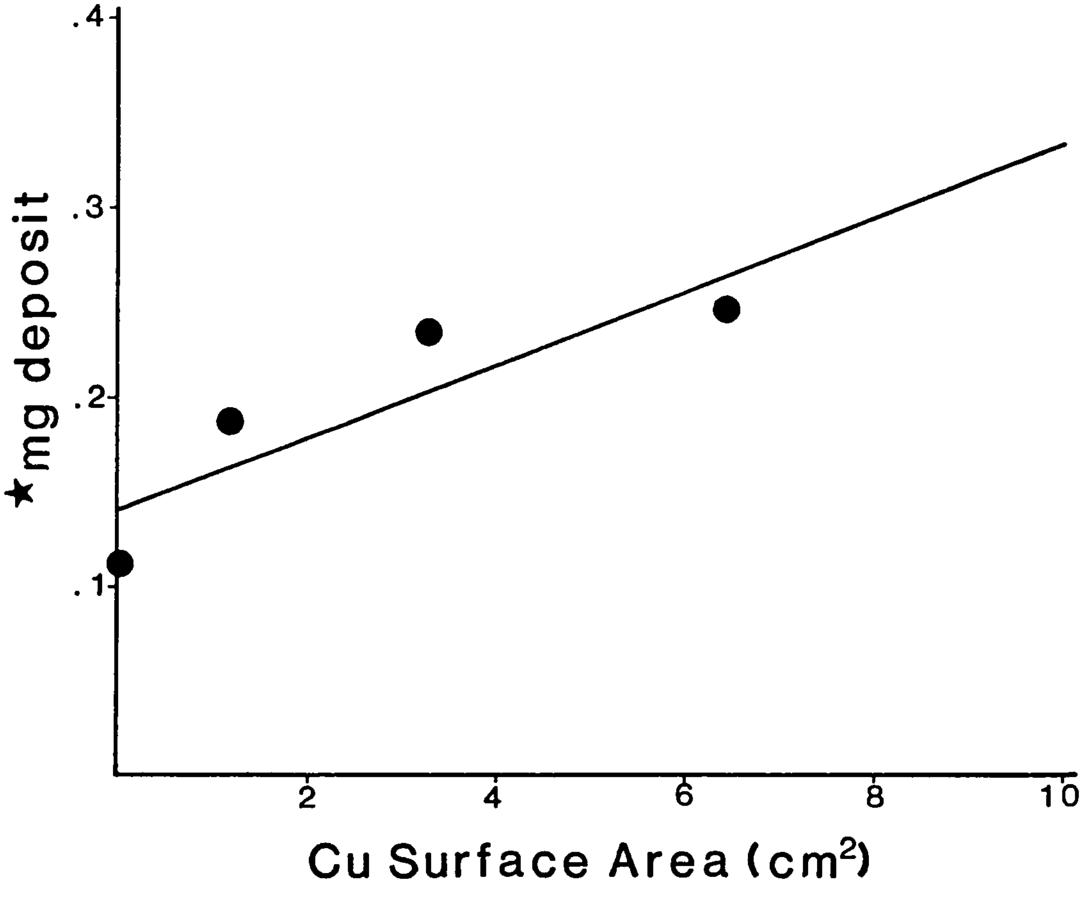


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FIGURE 27

Effect of $Cu(acac)_2$ on Jet A

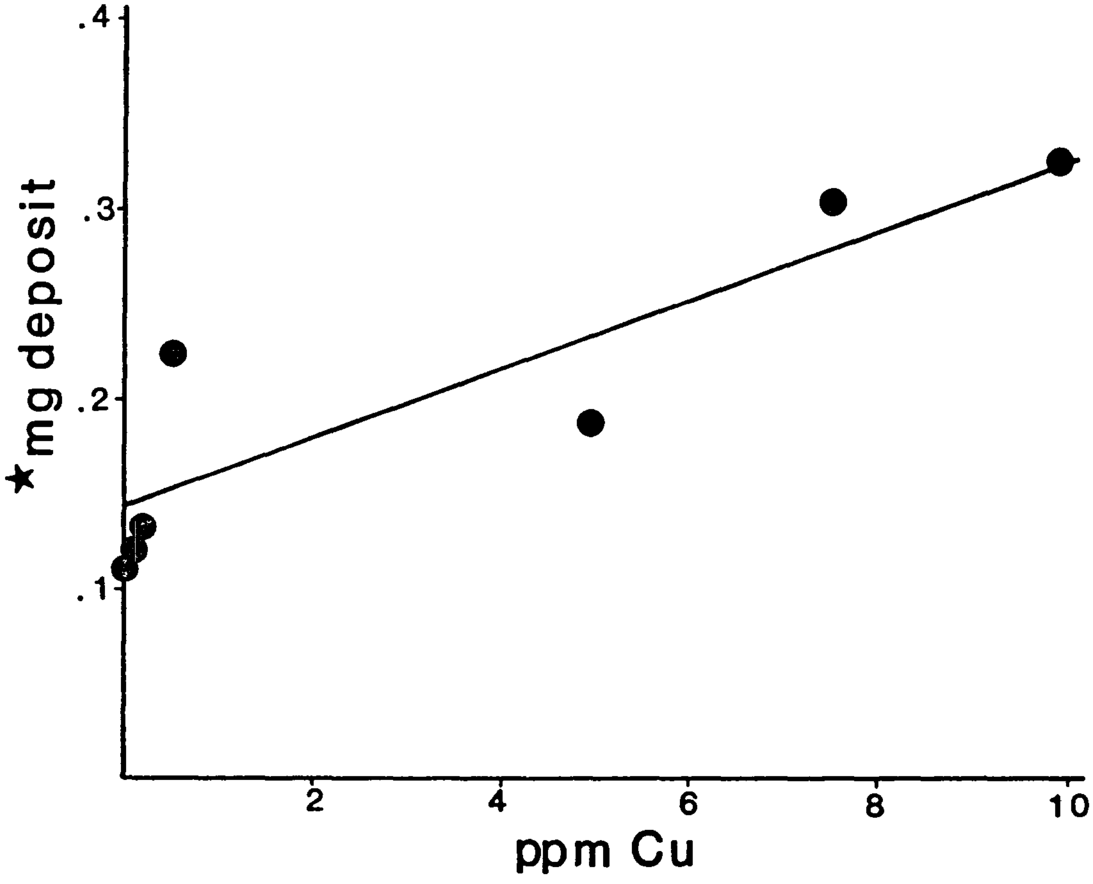

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FIGURE 28

Effect of Aging on Jet A. Analysis by HPLC

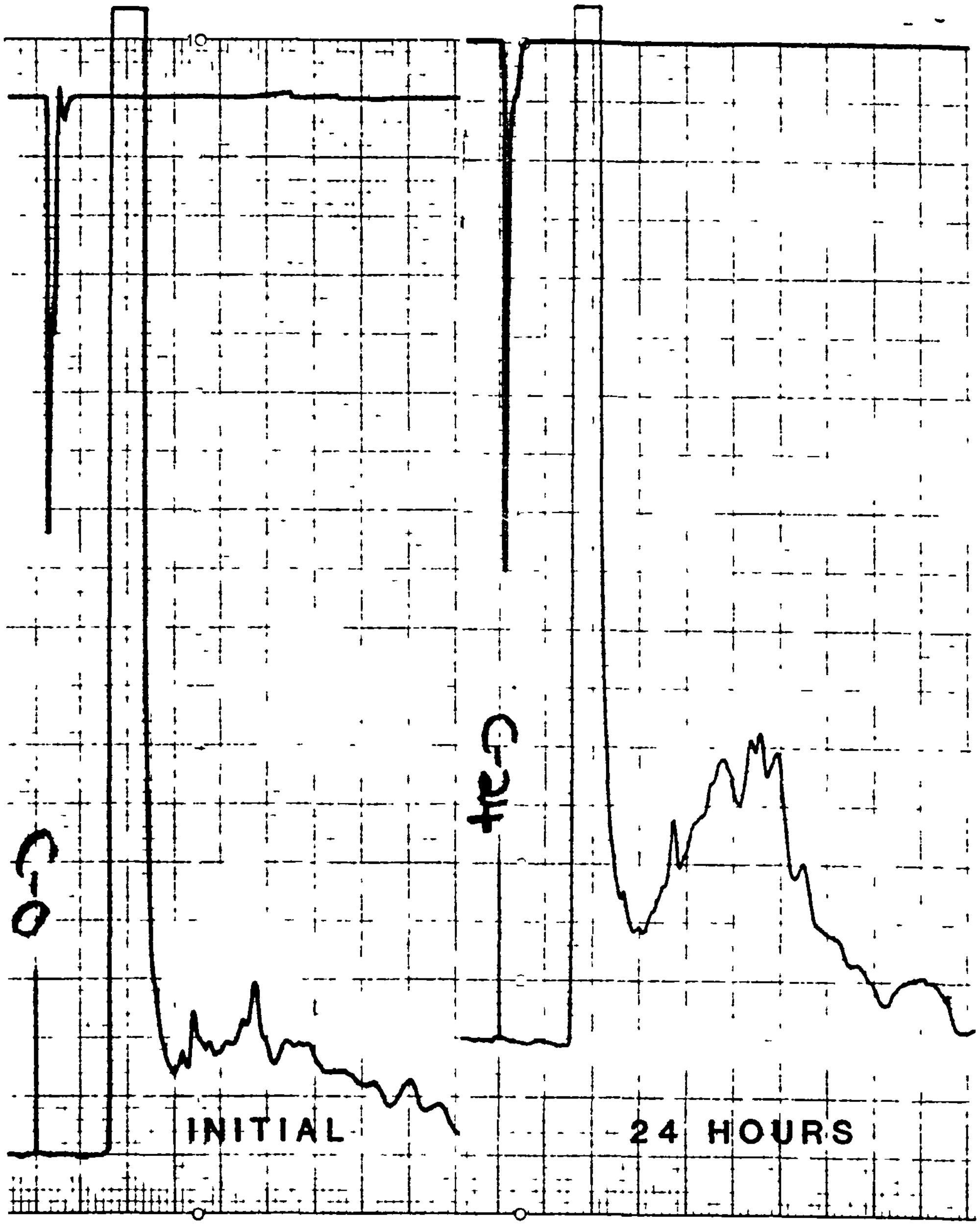


FIGURE 28.

Effect of Aging on Jet A.
Analysis by HPLC

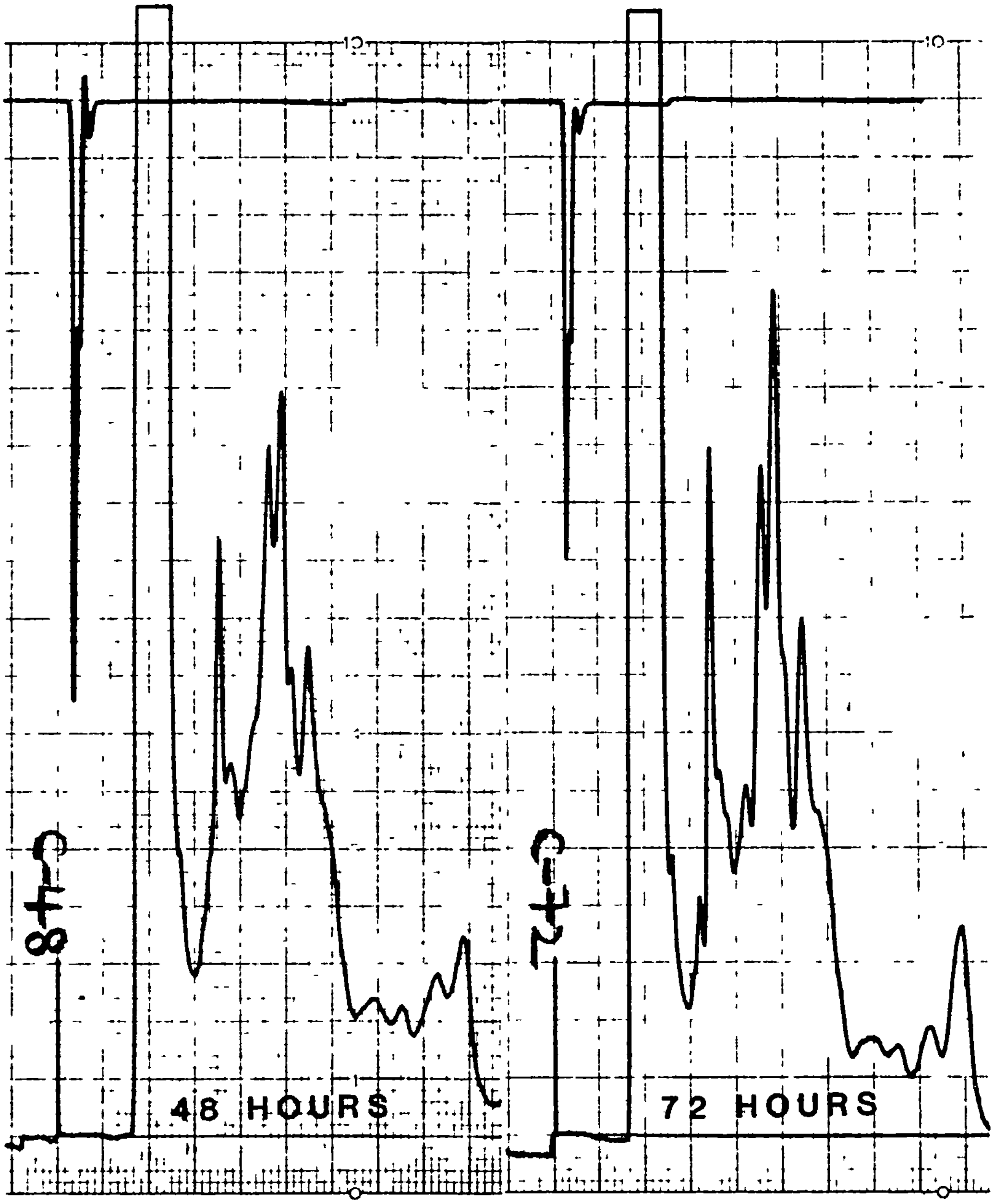


FIGURE 29
Comparison of Deposit Weight and HPLC Methods

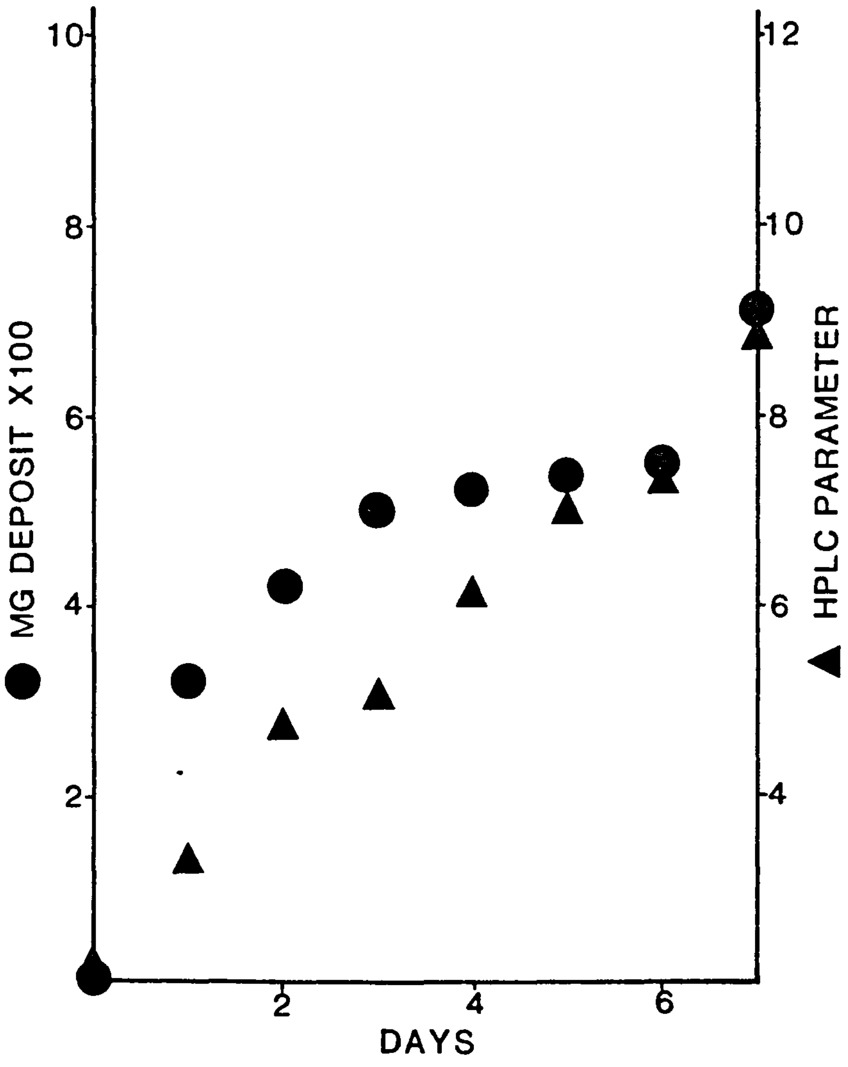


FIGURE 30

Effect of Aging on Fuel Dielectric Constant

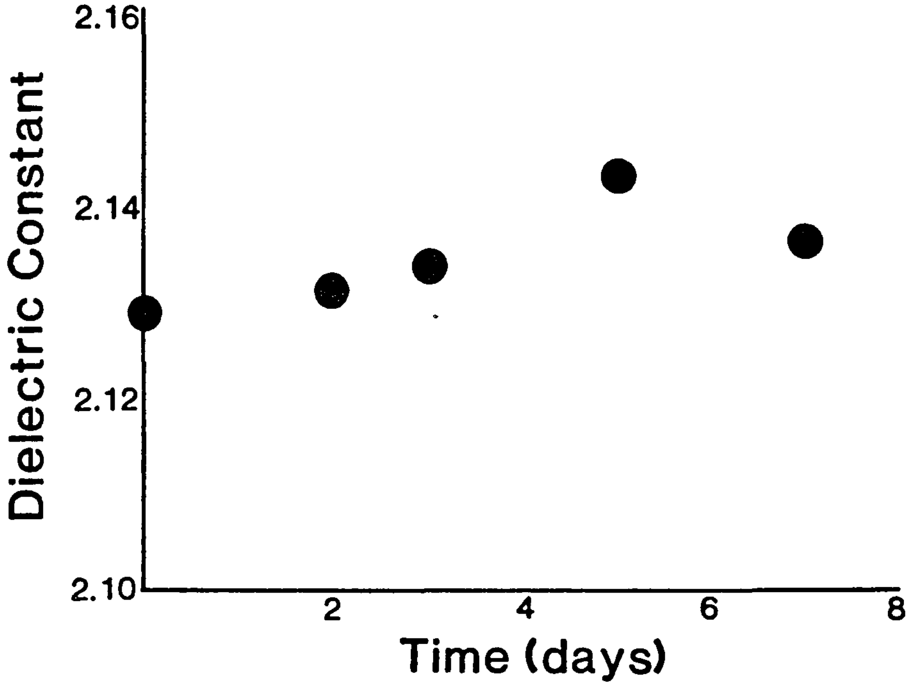


FIGURE 31.

Synfuels HPLC I

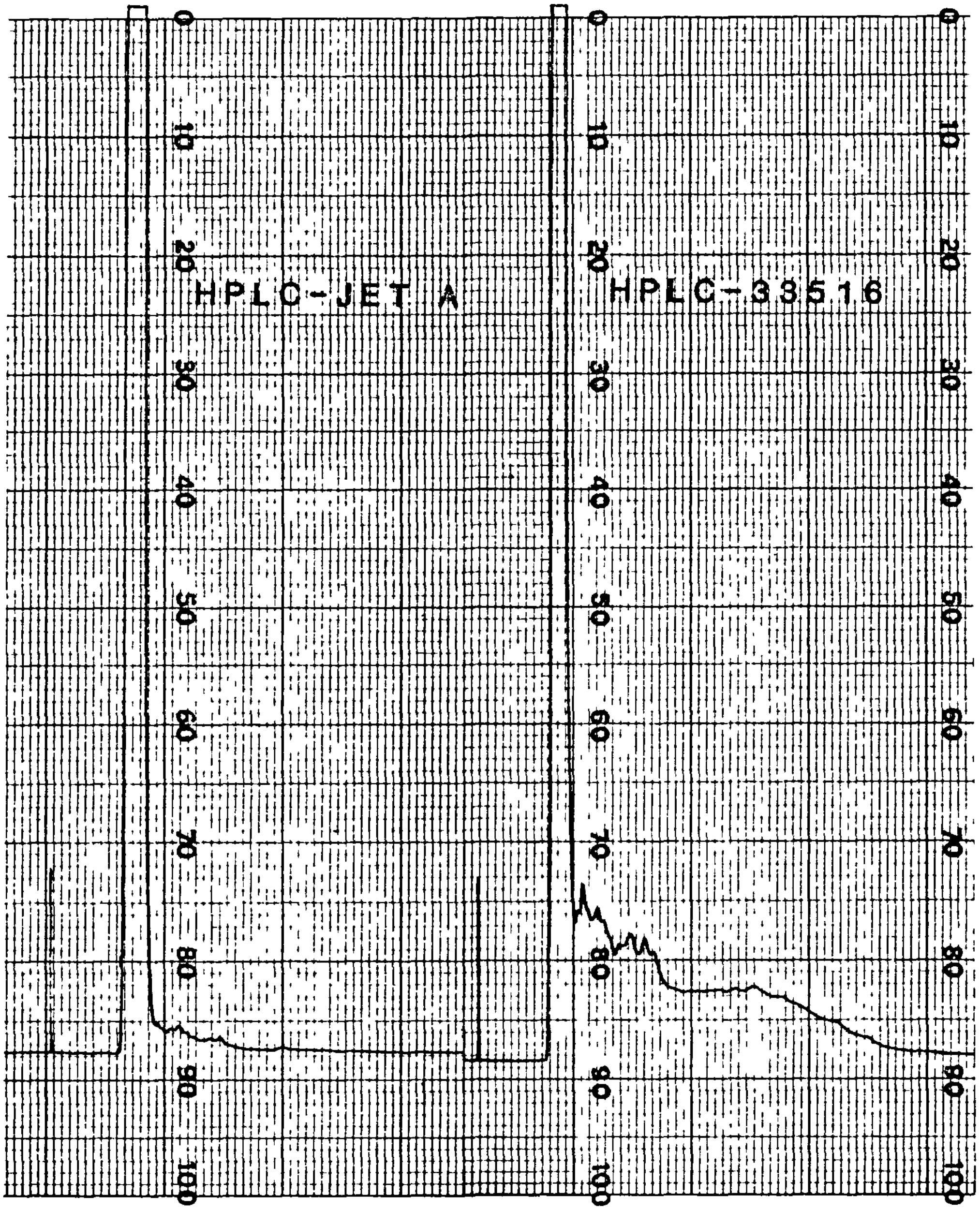


FIGURE 32

Synfuels HPLC II

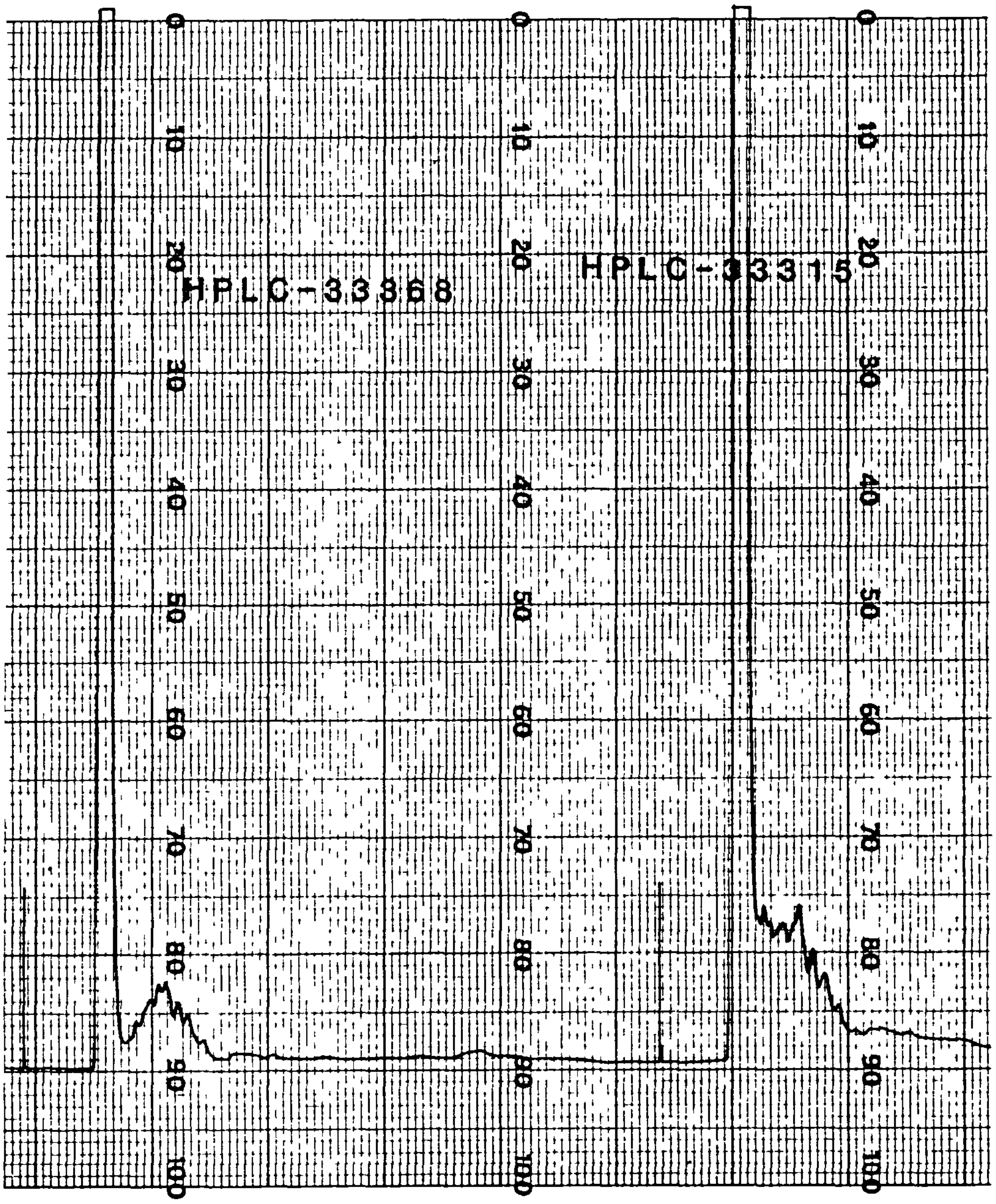


FIGURE 33.

Synfuels HPLC III

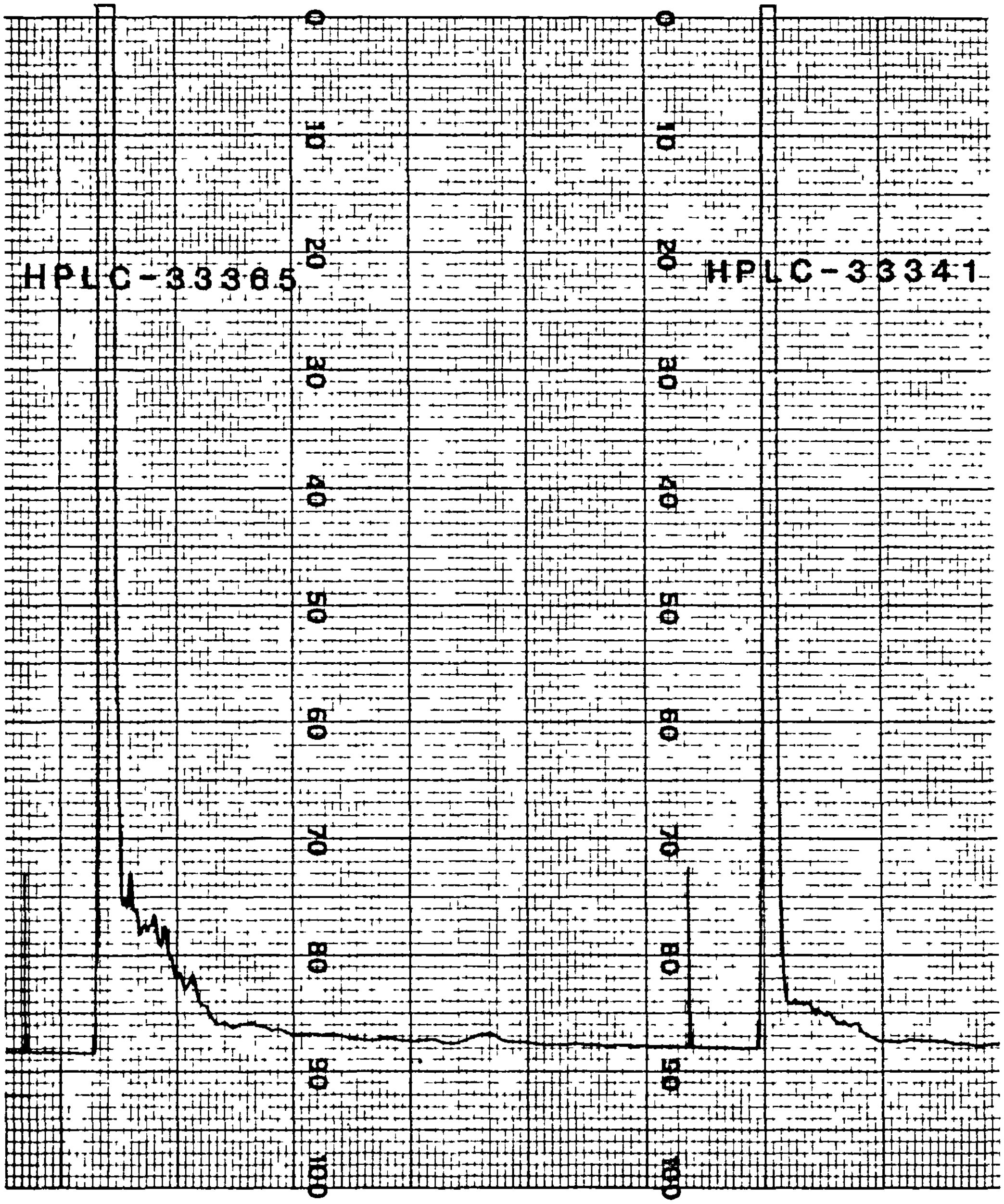


FIGURE 34.

Synfuels HPLC IV

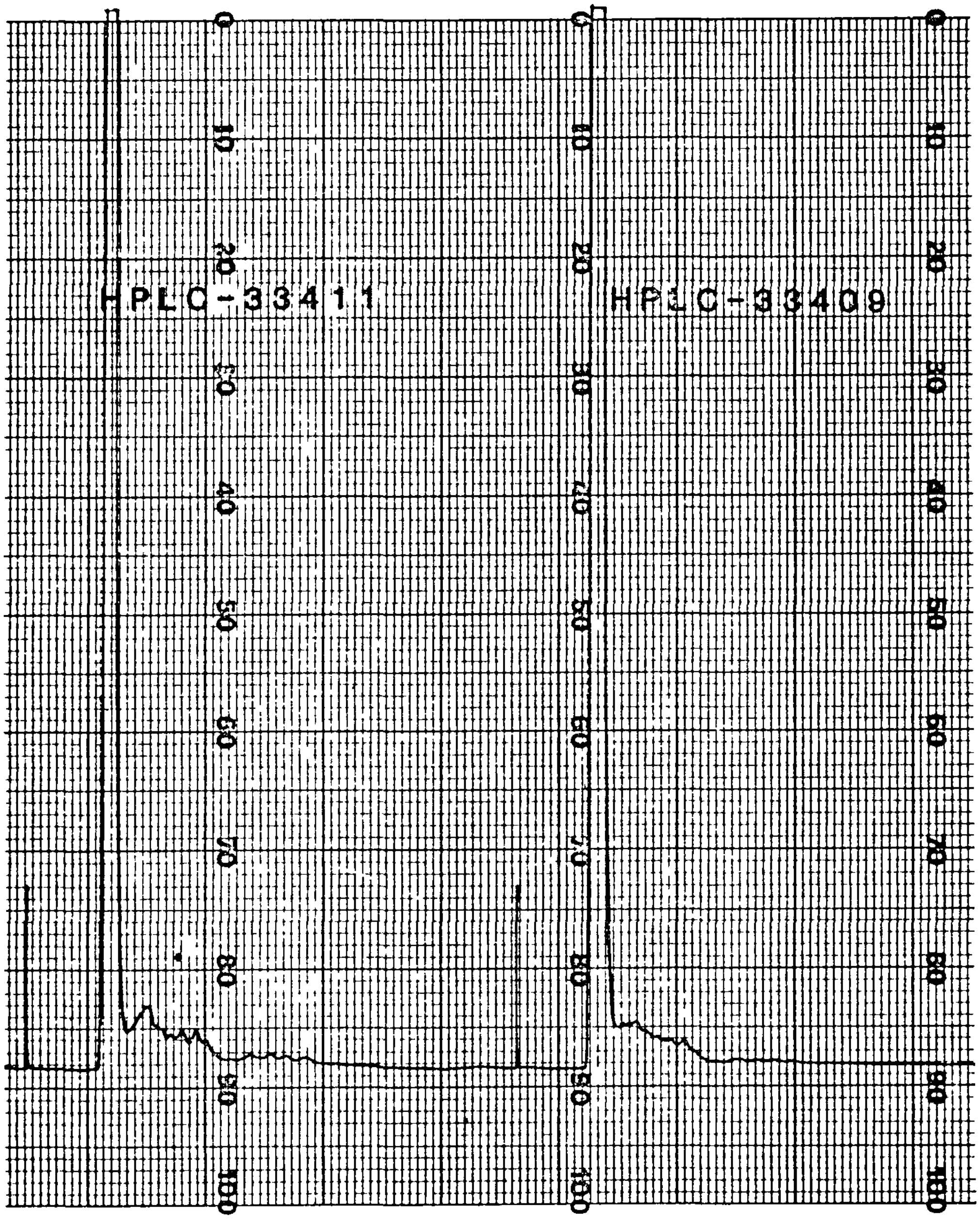


FIGURE 35

Synfuels HPLC V

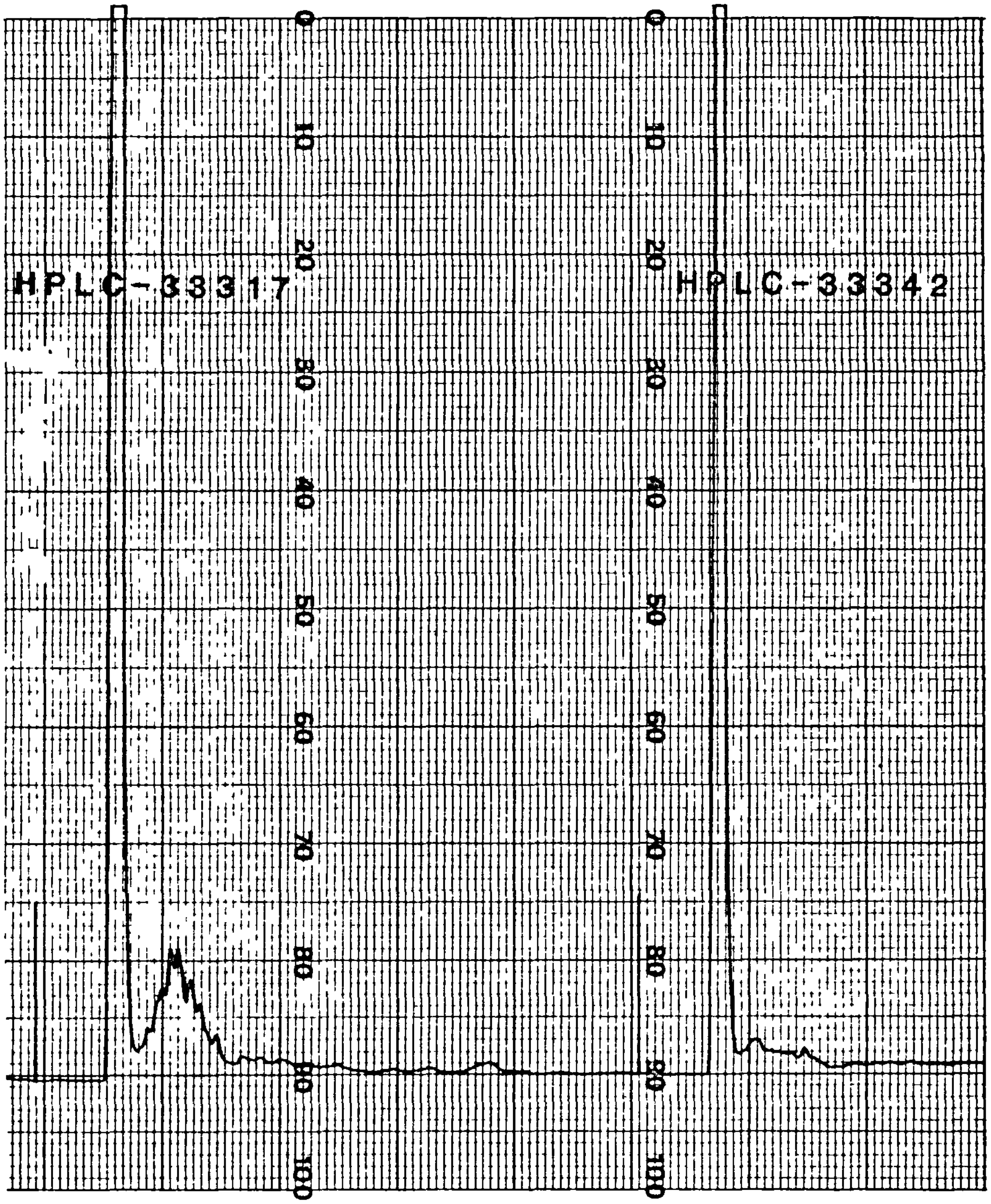


FIGURE 36

Effect of Aging on Synfuel. Analysis by HPLC

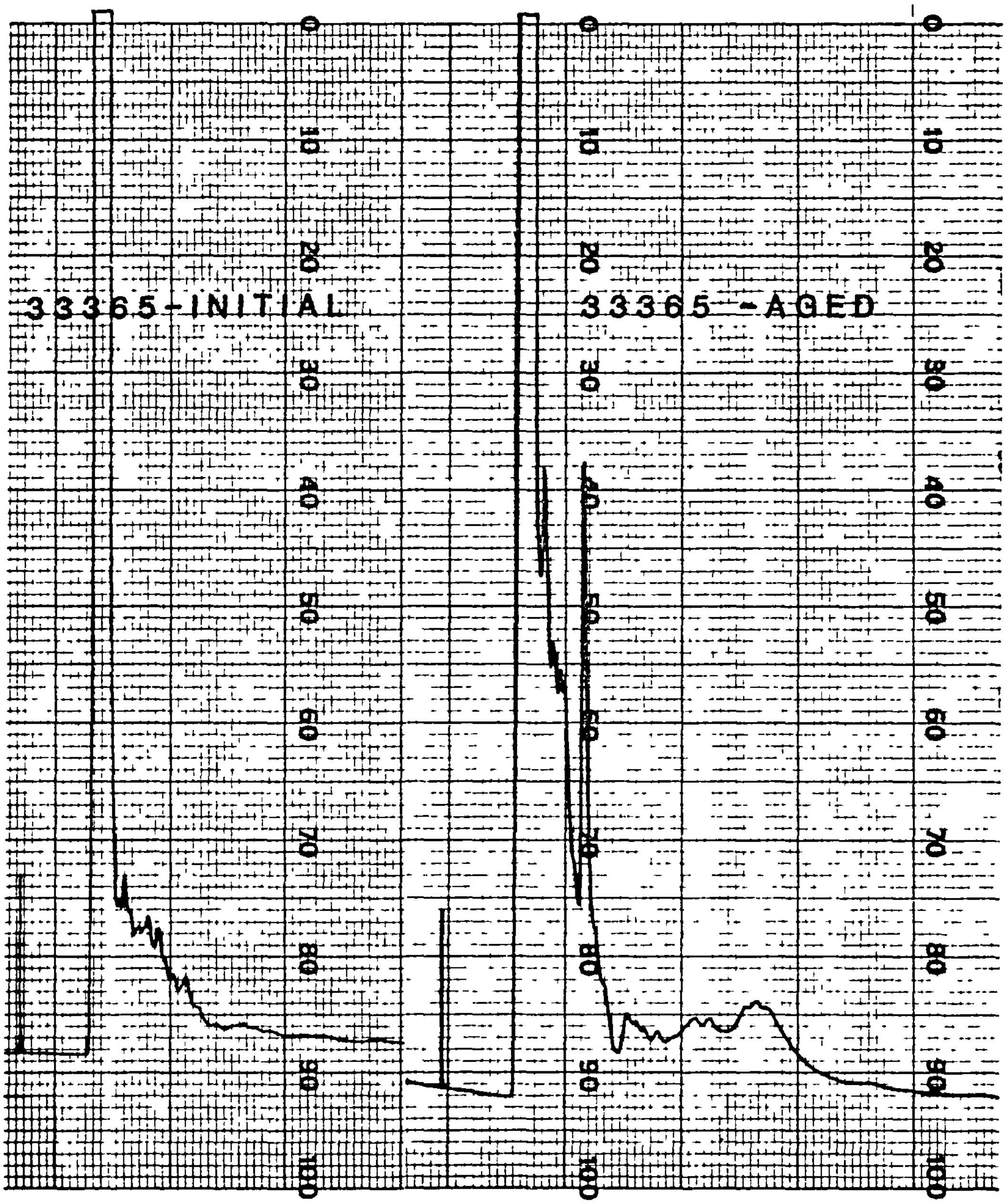


FIGURE 37

Synfuel Stability. Correlation with Existing Gum and Sulfur Content

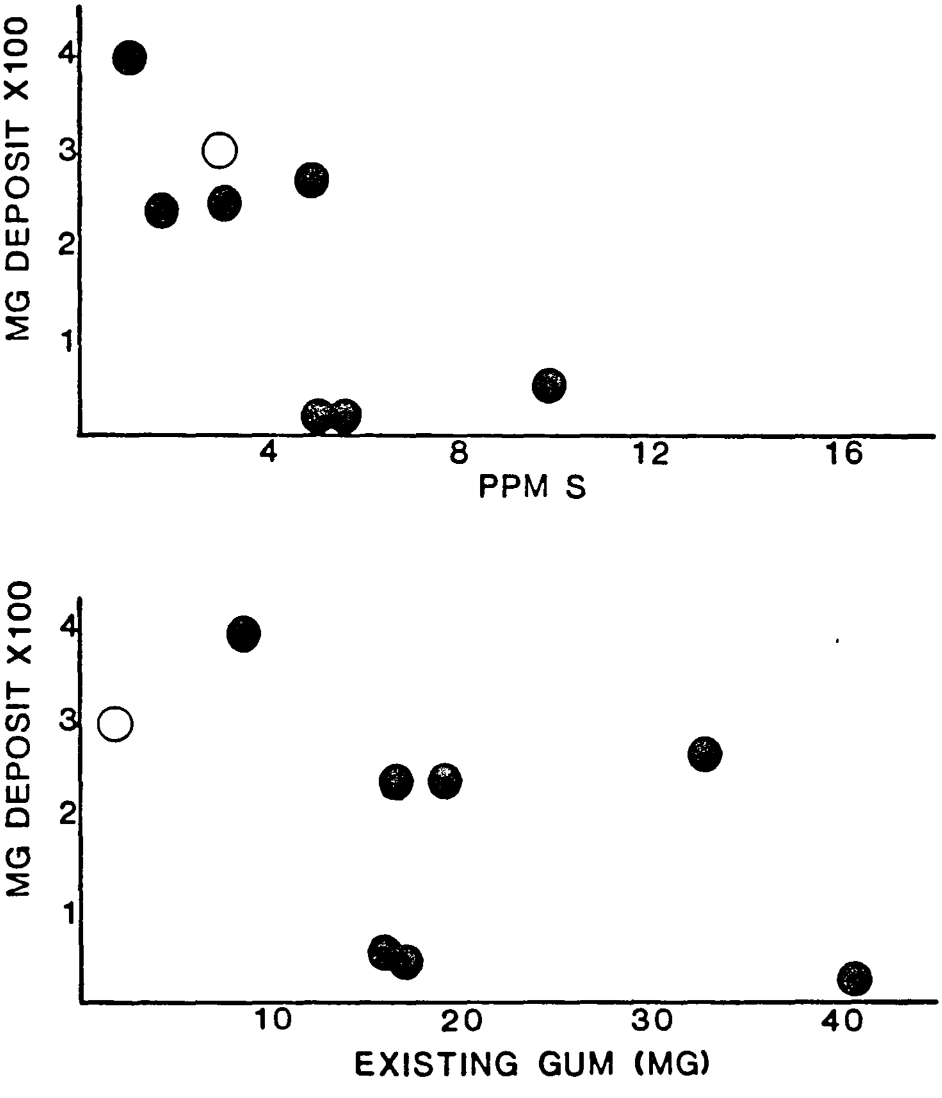


FIGURE 38

Synfuel Stability.
Correlation with
Aromatics and Nitrogen Content

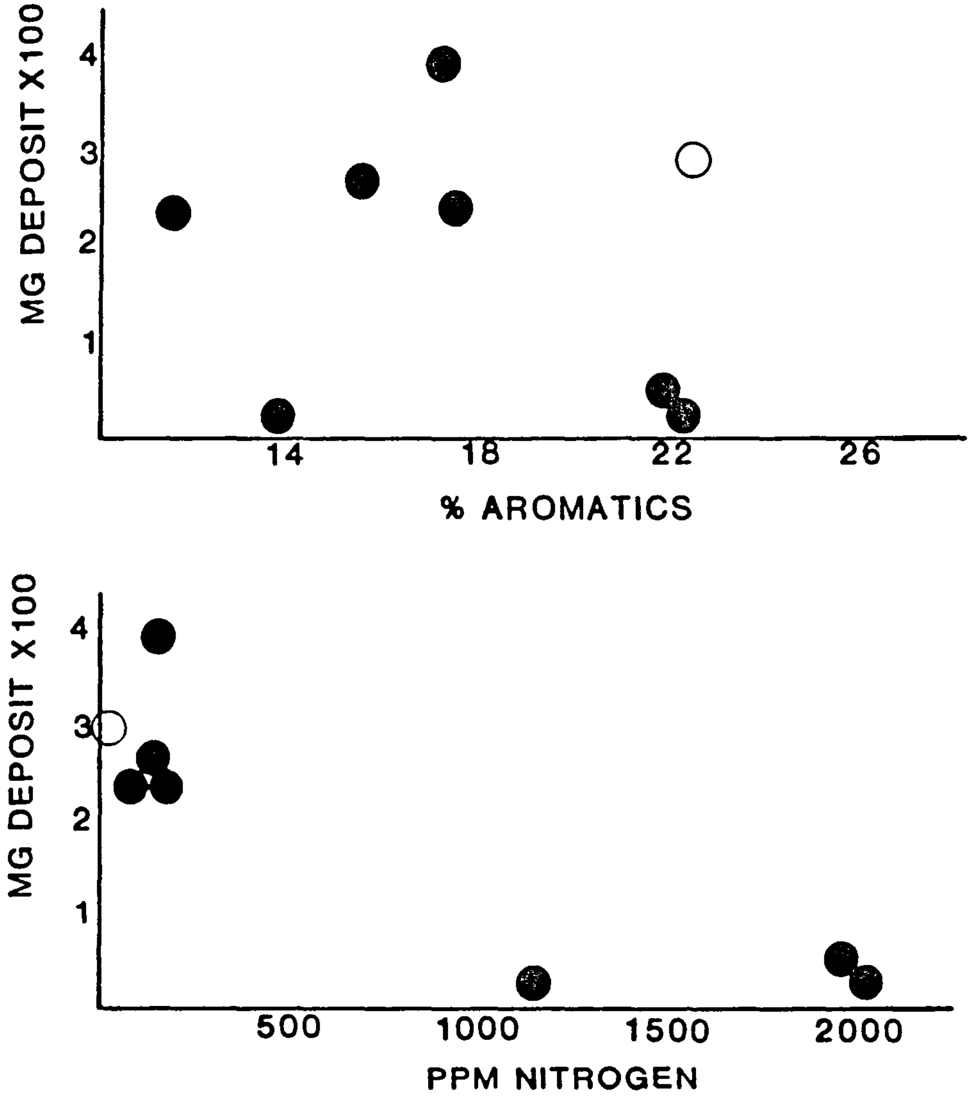


FIGURE 39

TRANSMISSION SPECTRUM OF MODEL SYSTEM STORAGE DEPOSIT

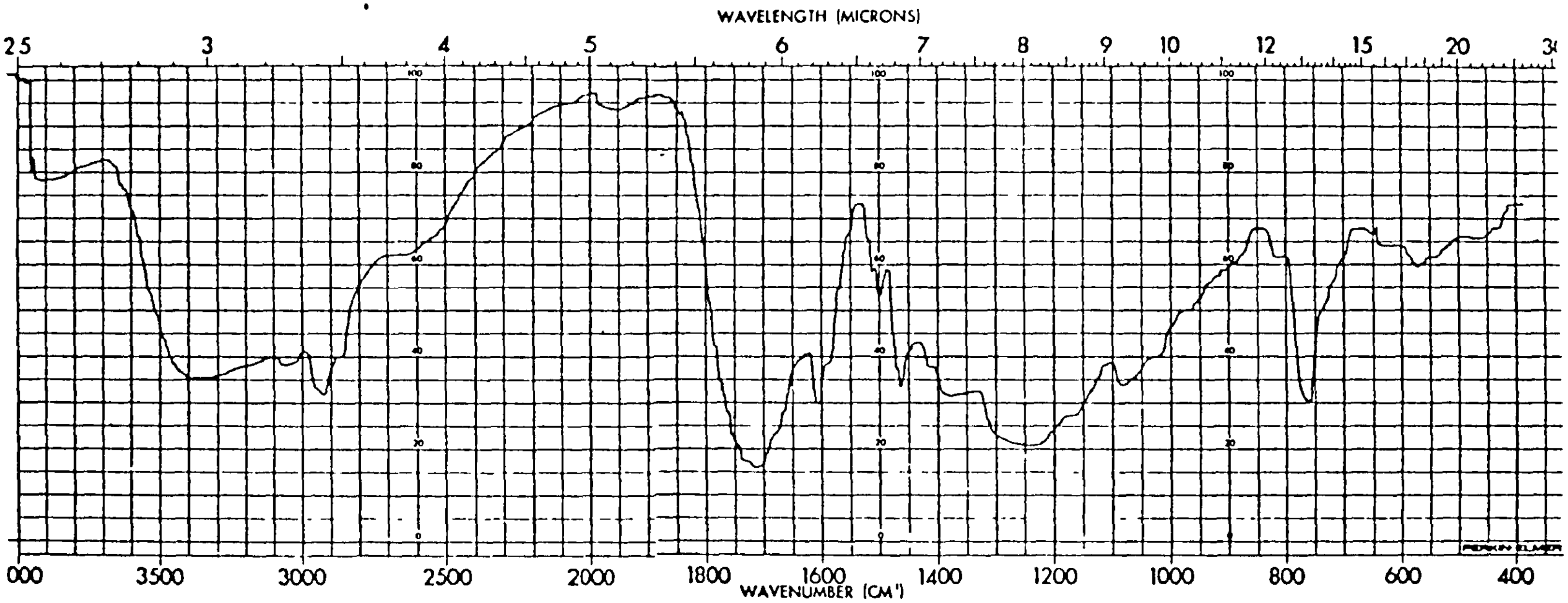


FIGURE 40

MULTIPLE INTERNAL REFLLCTANCE SPECTRUM OF MODEL SYSTEM STORAGE DEPOSIT

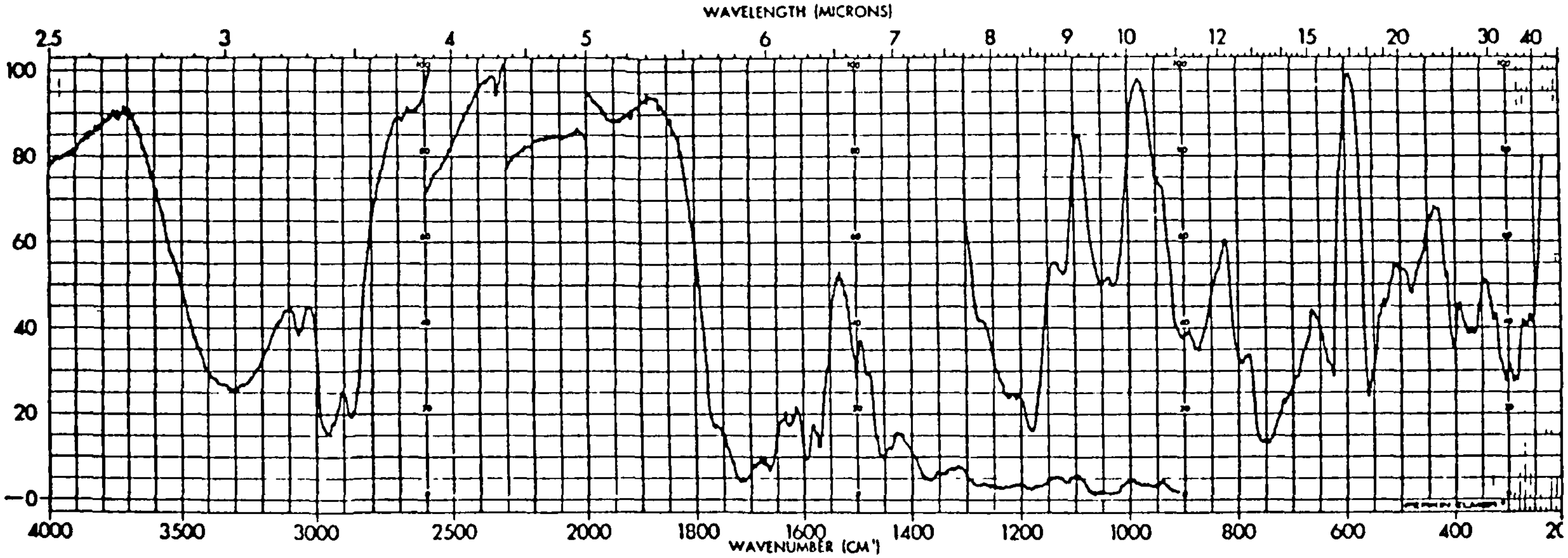


FIGURE 41

MULTIPLE INTERNAL REFLECTANCE SPECTRUM OF JET A STORAGE DEPOSIT

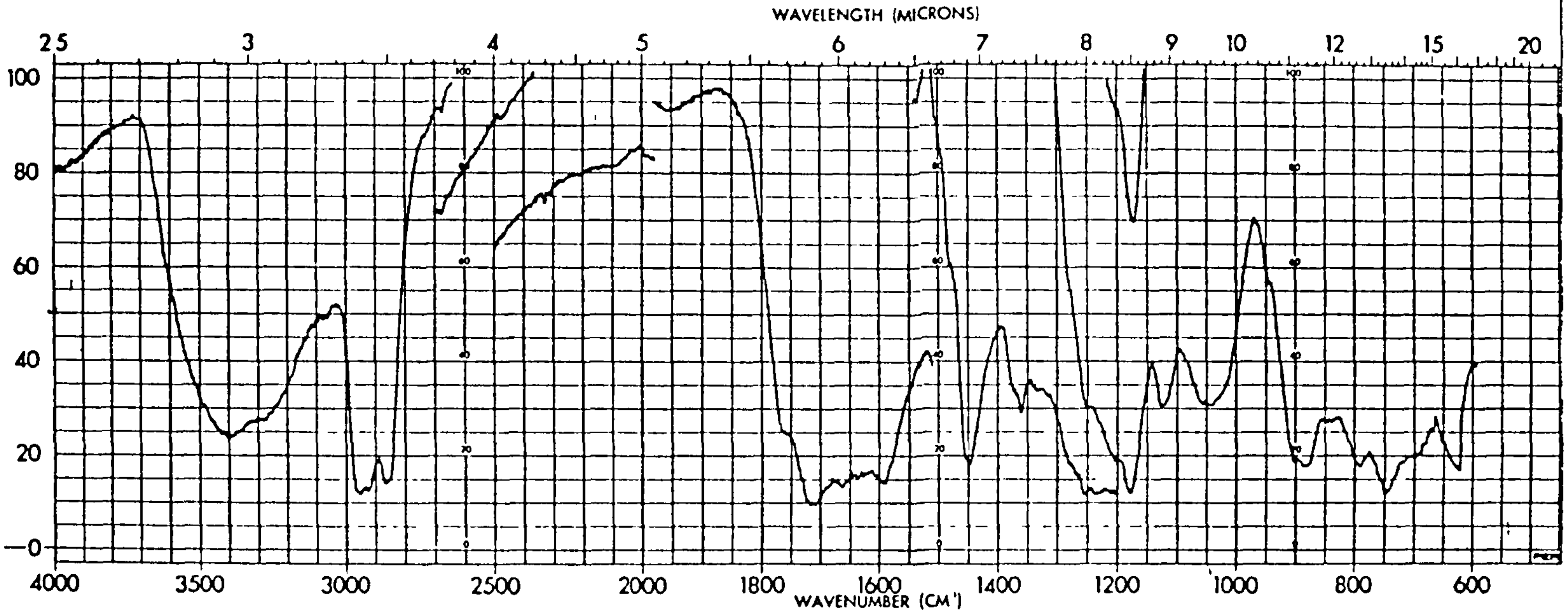


FIGURE 42

Jet A Storage Deposit
Gel Permeation Chromatogram

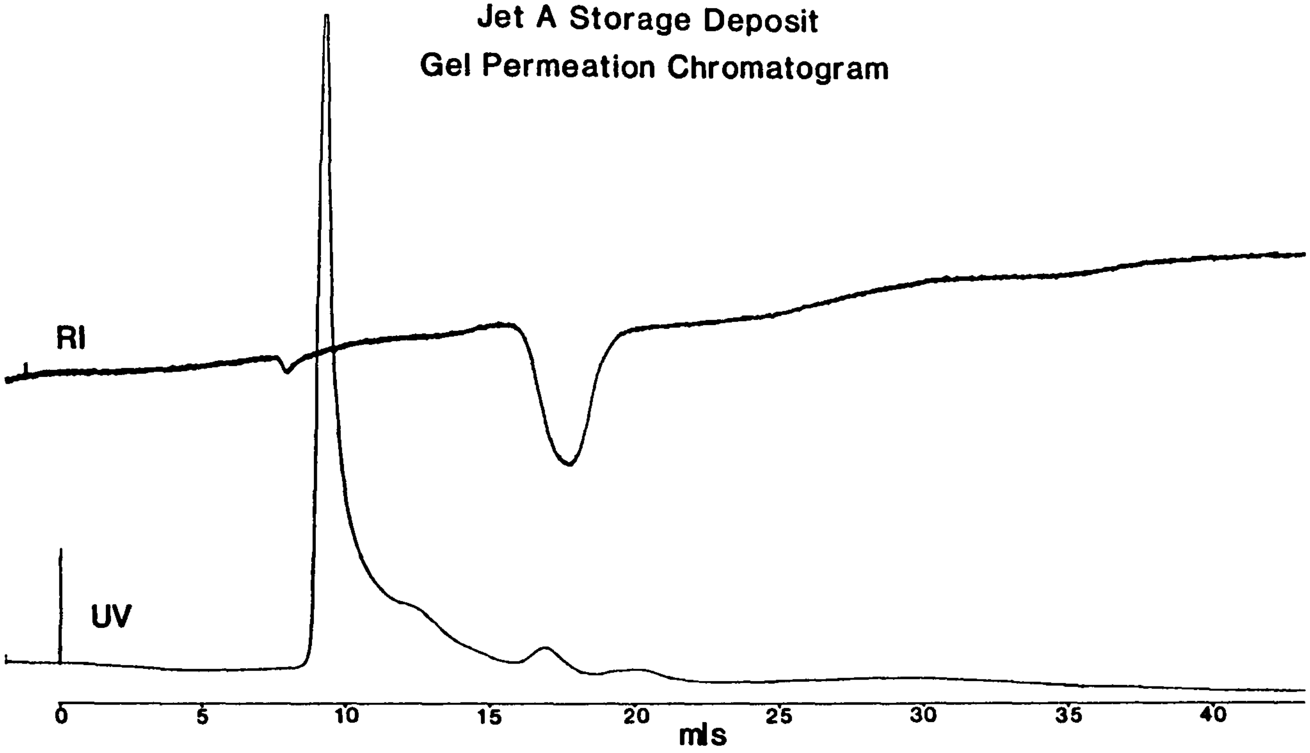


FIGURE 43
SIMS of Jet A Storage Deposit

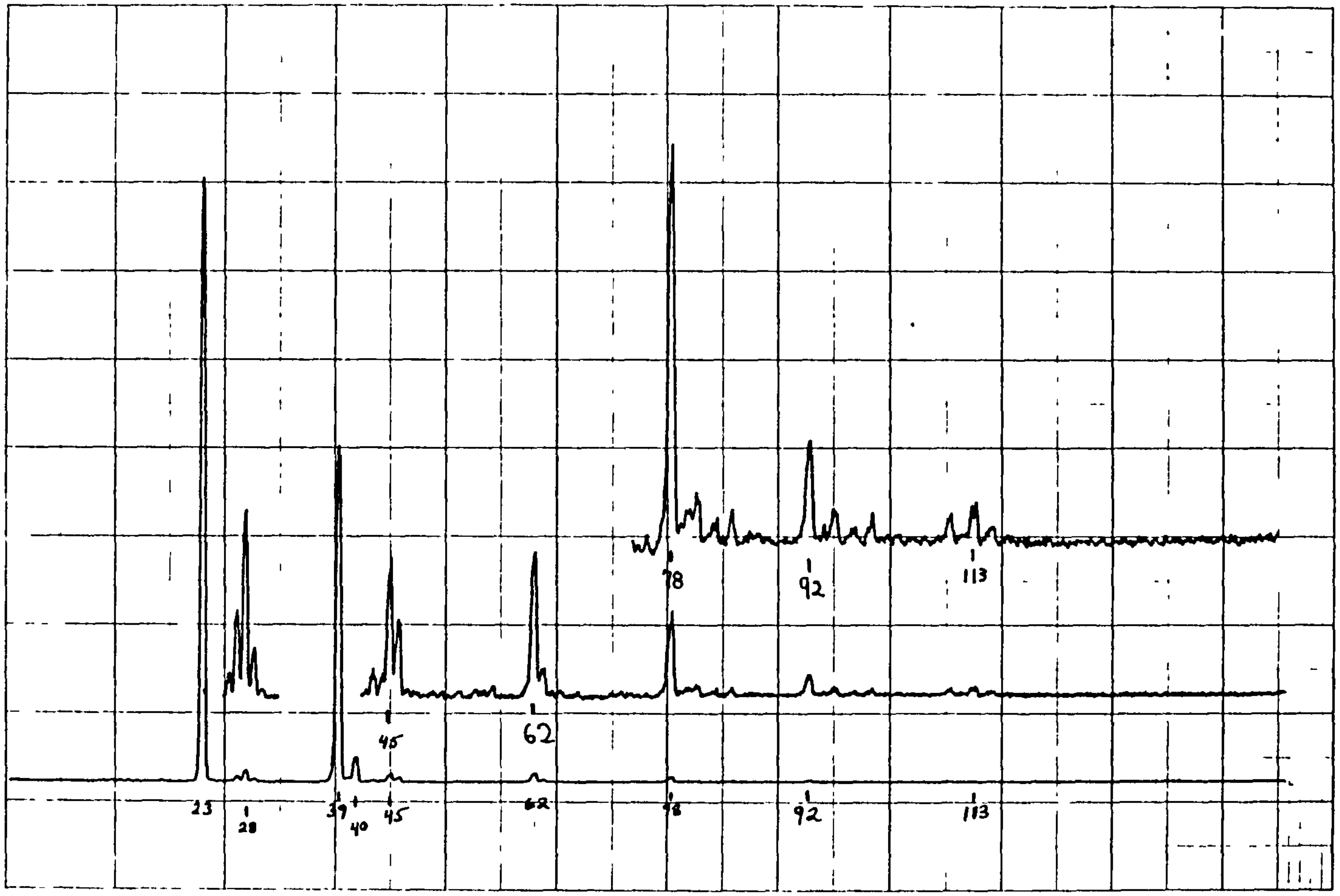


FIGURE 44
SIMS of Model Storage Deposit

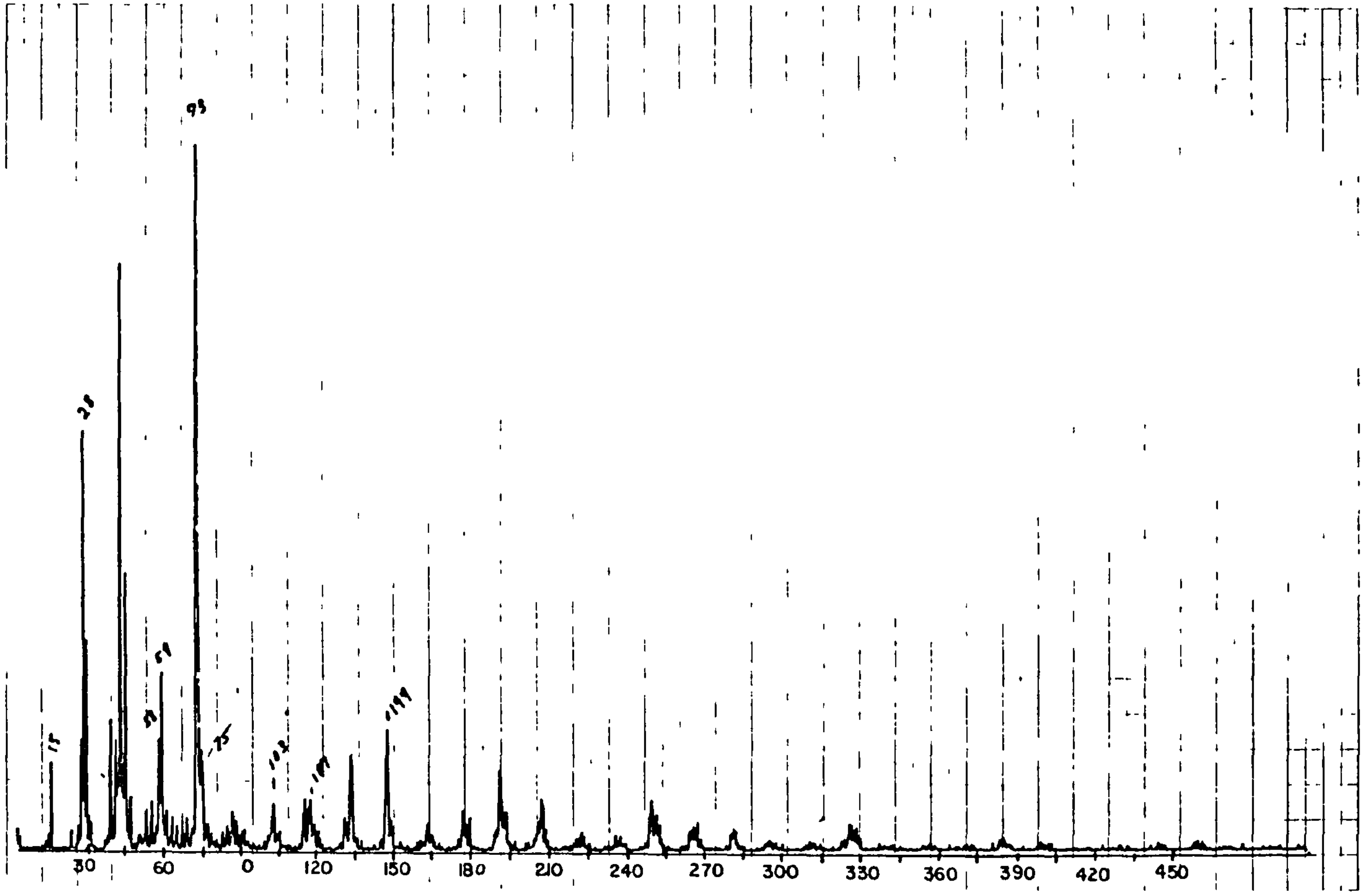


FIGURE 45

SIMS of Jet A Thermal Deposit - Initial

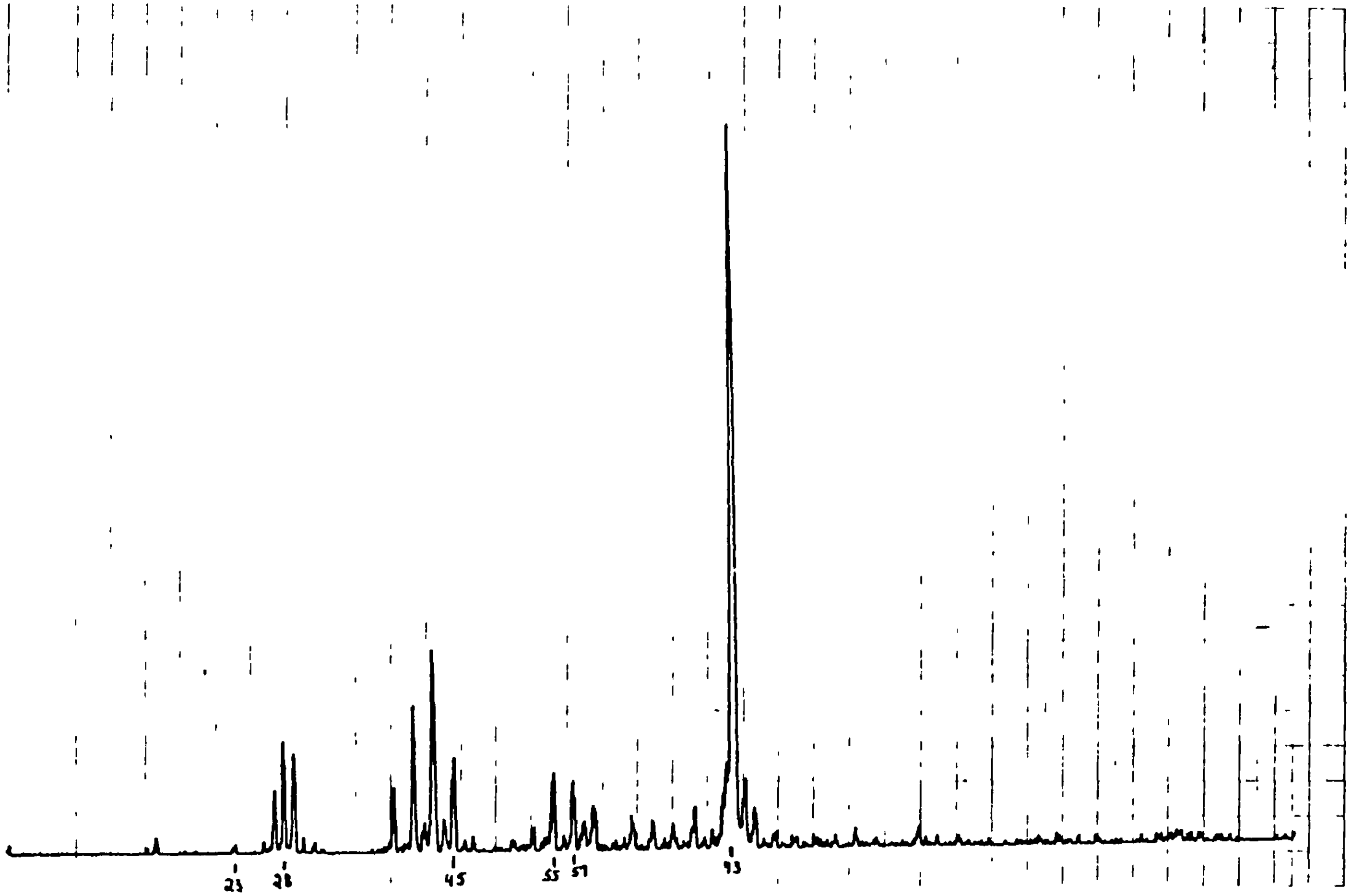
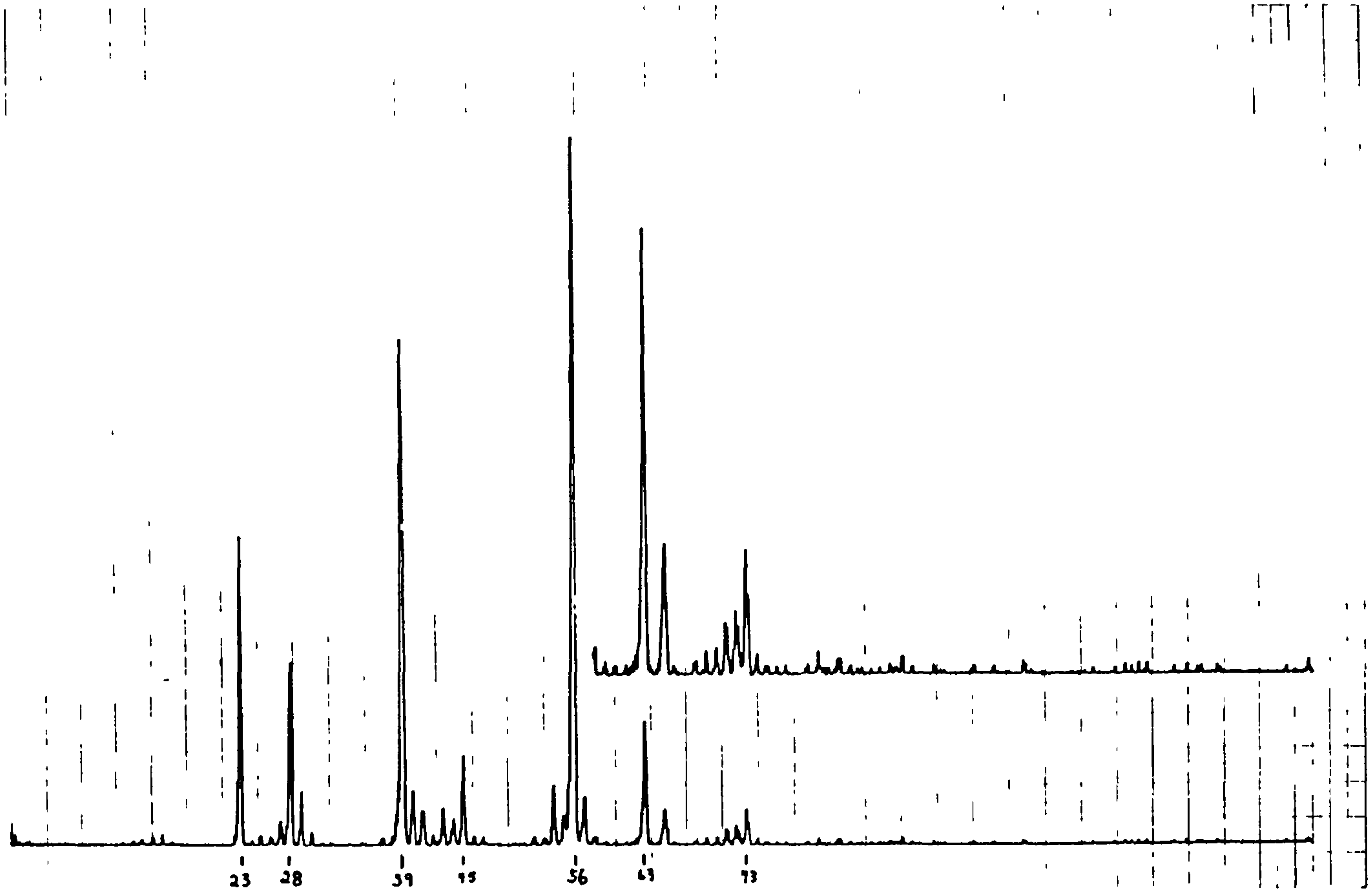


FIGURE 46

SIMS of Jet A Thermal Deposit - Final



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15 Supplementary Notes

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16 Abstract

The formation of insoluble deposits in a Jet A, a Diesel, and a model fuel (1/10 v/v tetralin/dodecane) was studied. Experiments were conducted using glass containers at 394 K with an air/fuel ratio of 14/1 The effects of addition of ppm levels of various compounds on deposit formation were evaluated. Nitrogen heterocycles were shown to produce a basicity-dependent acceleration of deposition Thiols and thiophene were shown to increase deposition while sulfides and disulfides act as inhibitors. Copper metal and its salts also promote deposition Results of various instrumental analyses of deposits and development of a high-performance-liquid-chromatographic method for monitoring deposit precursors are discussed

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