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Radiotracer Study of Turbine Aircraft Fuel Stability

By M. L. Whisman, F. O. Cotton, J. W. Goetzinger,
and C. C. Ward

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RADIOTRACER STUDY OF TURBINE AIRCRAFT FUEL STABILITY

by

M. L. Whisman,[1] F. O. Cotton,[2] J. W. Goetzinger,[3] and C. C. Ward[4]

ABSTRACT

The Bureau of Mines developed a radiotracer method (was developed) for detecting the contribution of selected components and additives to thermally induce deposits of turbine aircraft fuels. Fuels were examined before and after 52 weeks of storage at 130° F. Of particular concern was the influence of aromatic hydrocarbon fuel constituents on thermal-stability quality of jet fuels during storage. A microfuel coker test apparatus was used to thermally stress the test fuels and blends, and the resultant contribution to deposits of selected fuel components, labeled with carbon-14, was determined by radioactive-counting techniques.

Ninety-one blends of five test fuels with carbon-14-labeled fuel additives or components were prepared, tested, stored ~~for 52 weeks at 130° F,~~ and reanalyzed for deposit-forming tendency. These additives included two antioxidants, a metal deactivator, and a corrosion inhibitor. Of the labeled hydrocarbon fuel systems studied, the greatest reaction was observed in blends containing methyl- and ethyl-substituted indenes. Other aromatic types also showed some contribution to the deposits. ~~Three of~~ the additives showed a marked tendency to degrade and react during storage and thermal stress. A cresol antioxidant, however, barely contributed to deposit formation. Oleic acid interacted with cadmium present in aircraft fuel systems and produced deleterious effects upon the thermal-stability quality of the fuel.

INTRODUCTION

The Bureau of Mines, through a previous contract with the Air Force, had evaluated various methods of measuring with radiotracers the contributions of individual fuel compounds to deposit formation in a variety of hydrocarbon jet

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fuels (7-10).[5] Evaluations indicated that some of those methods could be extended for determining, predicting, and possibly understanding the thermal-stability phenomena associated with turbine aircraft fuels.

A radiotracer method had been developed that extended the sensitivity of determinations to the parts-per-billion range, and the techniques had been applied, with excellent results, to test blends that were thermally stressed in a static 5-ml bomb (7). Because the results obtained from the static system did not always correlate with those from a dynamic system, such as the coker, some of the techniques developed were modified and extended for a microfuel coker test (11) so that results would more closely simulate results obtained from a standard coker apparatus and would thus be more applicable to supersonic aircraft fuel systems. The present study includes this modified procedure and some test results.

Portions of some fuels used in this study were depolarized by percolation through a column of silica gel. Some were intentionally contaminated with red iron oxide (Fe_2O_3) and water for the purpose of observing the effects of these treatments upon thermal stability, both before and after storage of the unblended fuels. A high proportion of the radioactive fuel components selected for study was aromatic in nature. These included two substituted indans, two indenes, tetralin, a naphthalene, and a tetrasubstituted benzene. The significance of thermal degradation of jet fuel additives prompted the inclusion of two antioxidants, one metal deactivator, and a corrosion inhibitor in the study of thermal-stability characteristics. Important in the thermal-stability investigation was the determination of the extent and rate of loss of these additives in several fuel environments at high temperatures, as well as identification of the thermally induced degradation products. This report includes (1) the modified radiotracer procedures that were developed, (2) a description of the fuels and test blends studied, and (3) a summary of test data.

EXPERIMENTAL APPARATUS AND PROCEDURES

Development of Test Procedures

A microfuel coker test unit was obtained and installed in the Bureau of Mines radiochemical facility at the Bartlesville, Okla., Petroleum Research Center to test the thermal stability of high-temperature hydrocarbon fuels by the use of an added radiotracer. Initial tests were performed with operational procedures developed by the University of Dayton Research Institute (UDRI) and reported by Kittredge (2-3). The excellent agreement between the data from the two laboratories indicated satisfactory control of experimental parameters of the microfuel coker test equipment and procedures.

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[5] Underlined numbers in parentheses refer to items in the list of references at the end of this report.

Microfuel Coker Modifications

Modifications to both the microfuel coker equipment and procedure were required for the evaluation of the contribution by selected jet fuel components and additives to preheater and filterable deposits. The major modifications to the test equipment included replacing the standard 1-μ stainless steel filter after the preheater block with a 25-mm-diameter cellulose ester filter with a pore size of 0.45μ. This filter was designated the test filter, and subsequent measurements were compared to a 0.45-μ filter that preceded the preheater section. A second major change to the apparatus was the inclusion of a micrometer-controlled stainless steel metering valve on a tee in the fuel line between the filter on the preheater block and the pump for the purpose of collecting 5-ml samples during the test. These "grab" samples were used in calculating material balances and for further recovery of filterable deposits. Decontamination between tests was avoided by inserting the sampling valve in the fuel line ahead of the pump.

Test Temperatures

A test temperature for each of the blends used in this study was selected to give the maximum amount of information per run. Because of radiotracer costs, space requirements for storing samples, and other space and economic factors, the procedure was limited to one test temperature for each blend. Therefore, it followed logically that each blend should be tested at the breakpoint temperature of the neat (as received) fuel determined in this laboratory. To facilitate comparison, depolarized and contaminated fuels were filtered through a 0.45-μ cellulose ester filter just prior to thermal-stability tests; therefore, the effects of contamination were not reflected in a change of thermal-stability characteristics until the contaminated blend had been stored at elevated temperatures for a relatively long time.

Measurement of Preheater Deposits

Several innovations were required to measure the amount of radioactivity deposited on the preheater tube and the radioactivity associated with deposits that could be filtered from the thermally stressed fuel. Principal among these innovations was the design and construction of a proportional detector that could be used to measure the radioactivity associated with deposits obtained on the preheater tube. Figure 1 shows a cutaway section of this detector. The operating voltage for this detector was 2,200 volts, and the counting gas used was P-10, a mixture of 90 percent argon and 10 percent methane. A counting efficiency of about 45 percent was obtained for preheater deposits in this detector configuration.

Filterable Deposits

Filterable deposits were collected on three separate filters. The first was an inline filter after the preheater block. The standard 1-μ stainless steel filter was replaced with a 0.45-μ cellulose ester filter. This modification was required because of difficulty in recovering or measuring radioactivity collected in the metal filters. A 5-ml "grab" sample was secured

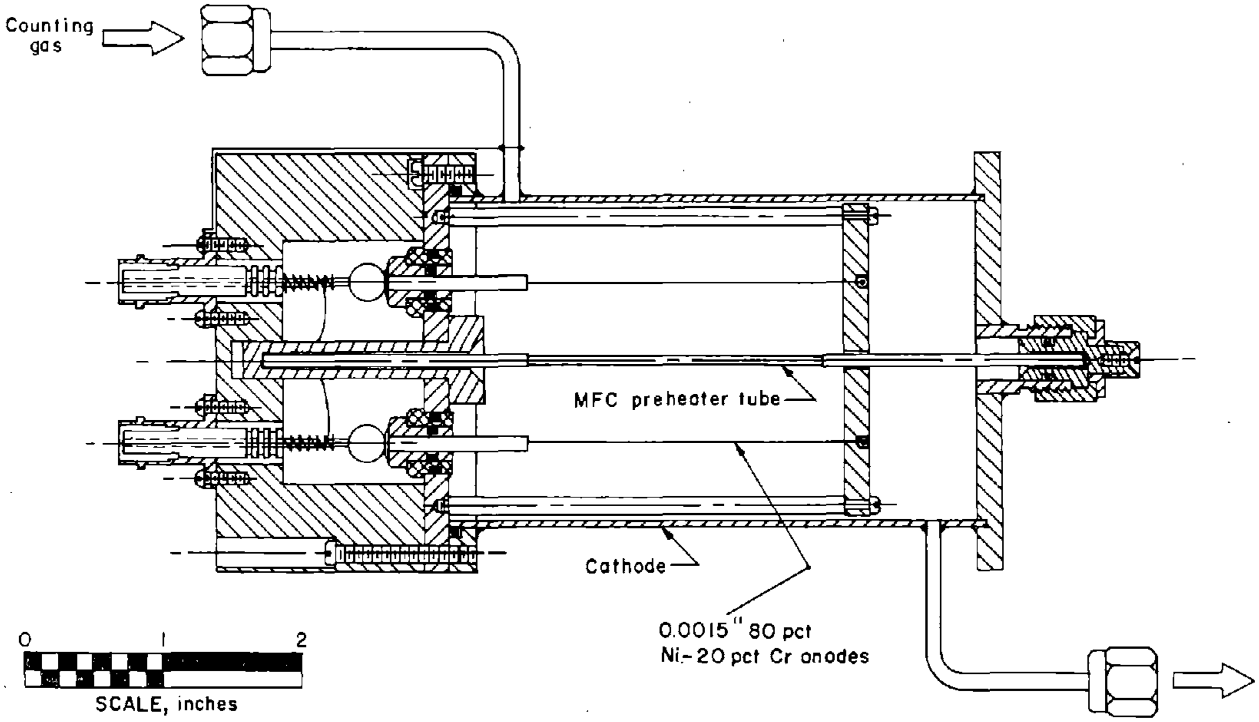


FIGURE 1. - Anticoincidence Detector for Microfuel Coker (MFC) Preheater Tubes.

through a micro metering valve 1 hour after the start of the test. This sample was passed first through a 0.30-µ cellulose ester filter and finally through a 0.010-µ filter. The total radioactivity on each filter was determined after rinsing the filter with n-heptane and then dissolving the filter in 1 cm^3 of acetone. The acetone solution was combined with 14 cm^3 of liquid-scintillation-counting solution, and radioassay was made by liquid-scintillation spectrometric techniques. To minimize errors associated with residual fuel left in the filters, each test filter was compared with a blank filter through which an equivalent aliquot of unheated test blend had been passed. Radioactivity material balances were determined by radioassay of an aliquot of unheated and unfiltered test blend by liquid-scintillation techniques and compared with a similar analysis of the heated and filtered blend.

Fuels and Fuel Treatments

Five fuels were selected for study. These fuels were stored in drums at 40° F under a blanket of helium. Working samples were obtained from a container by displacement with low-pressure helium. Unaltered fuels are referred to as "neat."

A portion of each of the five test fuels was depolarized by percolation through silica gel to remove 1 to 2 percent of the fuel that consisted of highly polar sulfur, nitrogen, and oxygen compounds. The bench-scale procedure used for this treatment was as follows: A 2-inch-diameter glass column was filled with an appropriate amount of chemical-grade 923, 100- to 200-mesh silica gel. A ratio of 1 g gel to 10 ml fuel was more than adequate for the gross separations desired in this treatment; therefore, in the depolarization of 3.5 gal of fuel, about 2,150 ml of gel was used. A flow rate of 1 liter/hr through the gel column was achieved by gravity pressurization to 5 psig with nitrogen. The last of the fuel was eluted through the column with isopropyl alcohol. To detect the interface between alcohol and fuel, a portion of carbon-14-labeled isopropyl alcohol was introduced into the column, and this was followed by 1 liter or more of unlabeled alcohol. Small fractions were collected from the zone between aromatics and colored polar materials, and each fraction was checked for radioactivity. Reconstitution of each fuel was guided by these radioactivity measurements, and the colored zone was identified as polar materials. It was desirable to omit both radioactive and colored material. In four of the treated fuels, about 1 percent of the fuel was discarded as polar material. More than 2 percent of the fifth fuel was removed by this treatment.

After depolarization was complete, each fuel was filtered through a 1.2-μ cellulose ester filter. This filtration was considered necessary because of the detrimental catalytic effect of gel contamination in depolarized fuels. The filtered fuels were blanketed with an inert gas and stored at 40° F.

The effectiveness of depolarization was checked by reprocessing an aliquot of the treated fuel through a small column containing a higher gel-to-fuel ratio. Color was the criteria for effective removal of polar materials.

Numerous test blends were contaminated by the addition of 20 ppm by weight of red iron oxide (Fe_2O_3) and water in a ratio of 1 part to 5,000 parts fuel by volume.

Preparation and Storage of Test Blends

Ninety-one blends of the five test fuels and nine carbon-14-labeled radiotracers were prepared, tested, and stored at 130° F. Each blend was stored for 52 weeks in amber glass bottles in a laboratory oven and then retested by the established procedures. Every 4 weeks each blend was removed from the oven and cooled to room temperature; depleted oxygen was replenished by blowing a metered amount of air over the surface of the blend. The position of each bottle in the oven was changed regularly to compensate for hot or cold spots in the oven.

Blend Components

Blends were prepared from aliquots of neat (untreated) test fuels as well as from portions that had been depolarized by the technique described. Still a third series of blends was prepared from neat fuel, contaminated as previously described.

Many of the radioactive fuel components selected for study are aromatic in nature. These included 1-ethylindan-3-^{14}C, 1-ethylindene-3-^{14}C, 1,2,3,5-tetramethylbenzene-^{14}C, 1-methylindan-3-^{14}C, 1-methylindene-3-^{14}C, 2-methyl-^{14}C-naphthalene, and tetralin-^{14}C. Aromatic compounds of these types are discussed by Kearns and coworkers (1). They showed, by a combination of fluorescent indicator adsorption and mass spectrometric analysis, that unstable jet fuels contain more of the indan and indene types than do stable fuels. In addition, Ward and Schwartz (4), in studying the storage stability of motor gasoline, found similar evidence that aromatic compounds are major contributors to storage gums and varnishes.

One paraffinic hydrocarbon, n-hendecane-1-^{14}C, and one diolefin, 1,5-hexadiene-1,6-^{14}C, were included in the selected fuel components so that their deposit-forming tendencies could be studied.

The study with fuel additives included two antioxidants, 2,6-di-t-butyl-^{14}C-p-cresol and N,N'-di-sec-butyl-p-phenylenediamine; oleic-1-^{14}C acid, a jet fuel component that apparently causes deposit formation by interaction with cadmium parts of fuel tanks; a metal deactivator, N,N'-disalicylidene-1,2-diaminopropane; and dilinoleic acid-^{14}C, the active ingredient of a corrosion inhibitor.

Gas Chromatographic Purification of Radiotracers

Organic materials labeled with carbon-14 are subject to self-decomposition promoted by the ionizing radiation of beta particles emitted from the decaying radioisotope. The self-decomposition of a compound labeled with a radioactive isotope can be caused by one or more of four effects: (1) internal primary radiation, such as disintegration resulting from the daughter atom of ^{14}C, which is ^{14}N; (2) external primary radiation, such as bond cleavages by beta particles; (3) secondary radiation, such as the reaction of a molecule with free radicals produced by ionizing radiation; and (4) chemical effects not necessarily associated with ionizing radiation.

Because of these changes in composition, it was necessary to purify each radiotracer just prior to use. Once diluted with a jet fuel or other solvent, self-decomposition of the radiotracer becomes insignificant because the energy from the emitted beta particles is absorbed by the fuel matrix. The decomposition of fuel molecules is insignificant because of the large volume of fuel used in each blend and the very short range of the beta particle.

The analytical tool used to purify the radiotracers was gas chromatography. Usually microdistillation or chemical crystallizations and extractions are required, and these procedures are difficult to apply to very small samples. However, a purification procedure was developed (6) that utilizes the efficiency and rapidity of gas chromatography and eliminates many of the disadvantages associated with other methods.

SUMMARY OF TEST DATA

Effect of Storage on the Thermal Stability of Fuels

Three samples of each of the five test fuels (neat, contaminated, and depolarized) were stored in bottles in a laboratory oven at 130° F for 52 weeks. Every 4 weeks each bottle was removed, cooled to room temperature, and aerated to assure an adequate supply of oxygen for oxidation reactions.

As each bottle reached the 52-week-storage interval at elevated temperature, it was removed, and microfuel coker tests were repeated to evaluate the effect of storage on the breakpoints. Table 1 is a tabulation of the data both before and after storage. No dramatic changes in breakpoint, as defined by the microfuel coker, were observed in any samples. The largest changes occurred in depolarized samples. Fuel 3-65-2, depolarized, increased in thermal-stability quality by an estimated 75° F, which was barely outside the analytical errors associated with the tests, while fuel 5-65-2, depolarized, deteriorated by about 125° F. These data fairly accurately show that neither contamination, depolarization, nor storage for 52 weeks at 130° F produce any appreciable changes in thermal-stability quality of the five high-temperature fuels, as defined by the microfuel coker.

Effect of Storage on Thermal Stability of Blends

Initial thermal-stability tests showed little or no contribution to deposits by the selected radiotracers, but after storage for 52 weeks at 130° F, several of the blends showed definite reaction and considerable contribution of the radiotracer to the deposits.

1-Ethylindan-3-^{14}C

Thermal-stability measurements and tracer tests on the 11 blends that contained the carbon-14-tagged fuel component 1-ethylindan-3-^{14}C showed no contribution of the radioactive indan to total deposits in the JP-5 fuel matrix (1-65-2) either before or after storage. The depolarized blends of this fuel, however, showed a twofold increase in total deposits from the indan. The contaminated blend of indan and this fuel showed the largest increase in indan contribution to thermally induced deposits. Although these were admittedly low-level reactions, the differences observed are believed significant. Blends of this radiotracer with the neat JP-6 (4-65-2) fuel showed a much larger extent of reaction and a 26-fold increase of tracer contribution to total deposits. The depolarized aliquot of fuel 5-65-2 also showed a fairly large reaction of the indan. A graphic presentation of the 1-ethylindan-3-^{14}C blends is shown in figure 2, and table 2 summarizes the data.

1-Ethylindene-3-^{14}C

Table 3 and figure 3 show the information obtained before and after 52 weeks of storage on 11 blends of jet aircraft fuel containing 1-ethylindene-3-^{14}C. This compound was reported by Kearns and associates (1) and by Ward and Schwartz (4) as being one of a type found in greater abundance in unstable fuels than in stable fuels; however, no other investigators had confirmed these findings in actual stability tests.

TABLE 1. - Breakpoints of neat, contaminated, and depolarized stored and fresh fuels, determined in microfuel coker

Fuel	Test temp, ° F, fuel-out/tube	Tube rating	Breakpoint, ° F	
			Stored 52 weeks at 130° F	Fresh
Neat:				
1-65-2	300/500	2	520	480
	310/520	3		
2-65-2	350/600	3	600	625
	360/620	4		
3-65-2	388/675	3	675	675
4-65-2	350/600	5	Est. 590	575
	338/575	1		
	342/585	2		
5-65-2	412/725	3	725	725
Contaminated:[1]				
1-65-2	290/480	1	500	480
	300/500	3		
	310/520	4		
2-65-2	362/625	5	610	625
	350/600	2		
	355/610	3		
3-65-2	388/675	3	675	675
4-65-2	338/575	1	Est. 610	575
	350/600	1		
	375/650	Est. 8		
5-65-2	412/725	4	710	725
	400/700	2		
	405/710	3		
Depolarized:				
1-65-2	320/540	5	500	540
	300/500	3		
2-65-2	330/560	2	600	560
	340/580	2		
	350/600	3		
3-65-2	370/640	1	Est. 725	640
	388/675	2		
	400/700	2		
4-65-2	370/640	8	Est. 610	640
	338/575	1		
	350/600	1		
5-65-2	400/700	8	Est. 620	750
	375/650	6		
	350/600	1		

[1] Contaminated with 20 ppm (by weight) Fe_2O_3 and 1 part water to 5,000 parts fuel (by volume).

TABLE 2. - Storage stability of blends containing 3 ppm of 1-ethylindan-3-^{14}C

Fuel	Treatment	Contribution of radiotracer to total deposits, percent		Radioactivity recovery, percent
		Before storage	After 52 weeks at 130° F	
1-65-2	Neat..................	0.060	0.037	98.5
	Contaminated..........	.000	.108	99.8
	Depolarized...........	.041	.075	100.4
2-65-2	Neat..................	.067	.015	99.8
	Contaminated..........	.015	.005	100.1
	Depolarized...........	.143	.029	99.2
3-65-2	Neat..................	.001	.027	100.0
4-65-2	Neat..................	.038	.988	99.2
5-65-2	Neat..................	.013	.083	101.4
	Contaminated..........	.048	.023	101.4
	Depolarized...........	.019	.654	96.7

TABLE 3. - Storage stability of blends containing 2 ppm of 1-ethylindene-3-^{14}C

Fuel	Treatment	Contribution of radiotracer to total deposits, percent		Radioactivity recovery, percent
		Before storage	After 52 weeks at 130° F	
1-65-2	Neat..................	0.140	0.068	99.9
	Contaminated..........	.080	.137	99.5
	Depolarized...........	.018	.044	98.6
2-65-2	Neat..................	.026	.124	100.1
	Contaminated..........	.129	.085	99.9
	Depolarized...........	.004	.121	99.9
3-65-2	Neat..................	.122	.080	101.5
4-65-2	Neat..................	.155	5.317	[1]95.9
5-65-2	Neat..................	.108	.560	102.4
	Contaminated..........	.096	.161	100.3
	Depolarized...........	.062	3.080	[1]92.5

[1] Reflects a loss of radioactivity during storage period.

Although, initially, no significant deposit contribution from this compound was observed or reported for these 11 blends, after 52 weeks of storage at 130° F, several of the blends showed definite and considerable reaction and contribution of the radiotracer to the deposits. None of the three blends containing contaminates in the form of red iron oxide (Fe_2O_3) and water showed any significant difference from neat fuel blends. However, one of three depolarized blends showed a large contribution to total deposits from the indene component. The poor radioactivity balance obtained on two blends shown in table 3 resulted from a change during storage rather than from a change during thermal-stability tests. In both cases, the specific radioactivity of the blend became lower during storage. Initially, it was thought that this apparent loss was caused by some of the radiotracer reacting to form insoluble

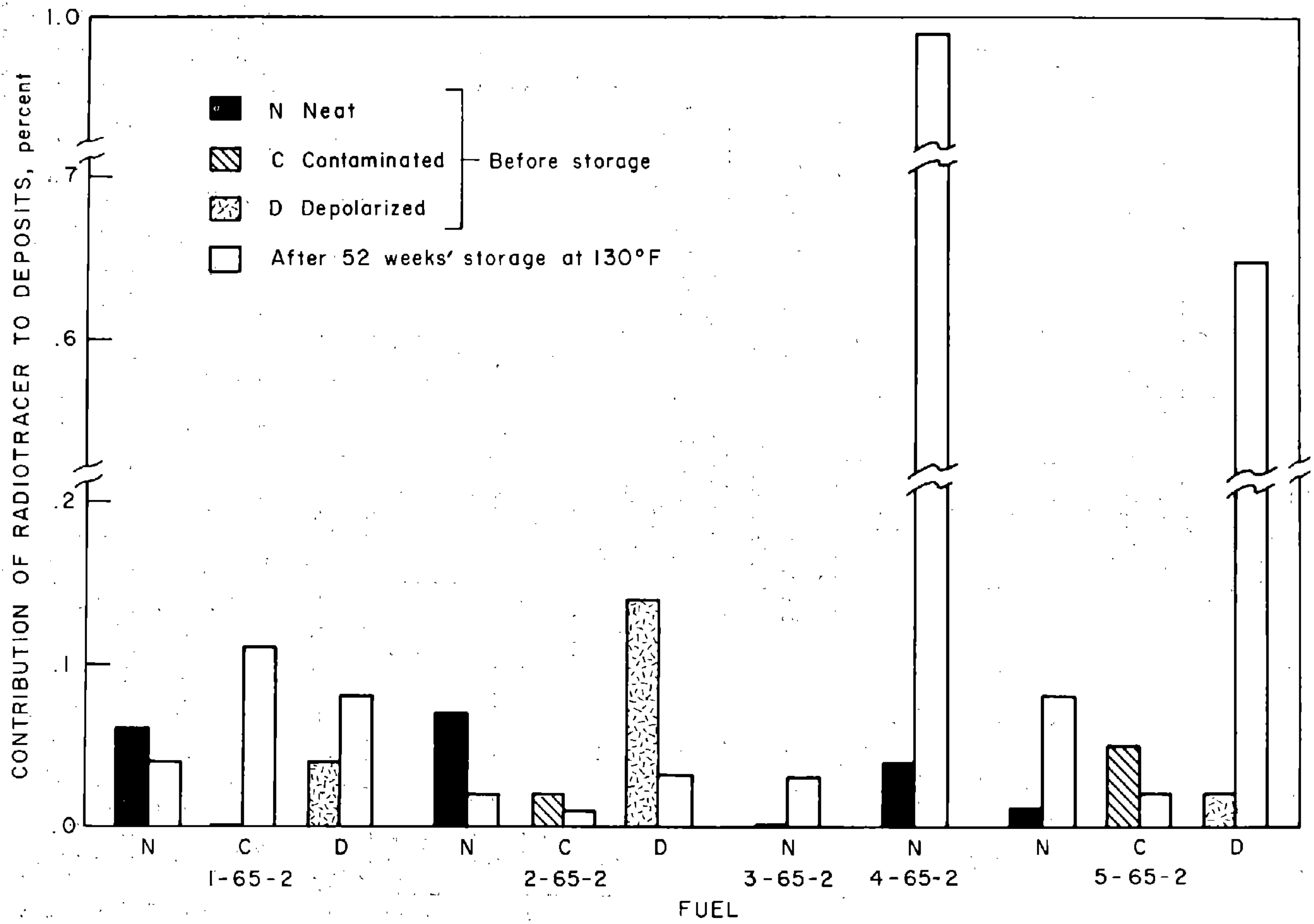


FIGURE 2. - Contribution of 1-Ethylindan-3-^{14}C to Total Deposits.

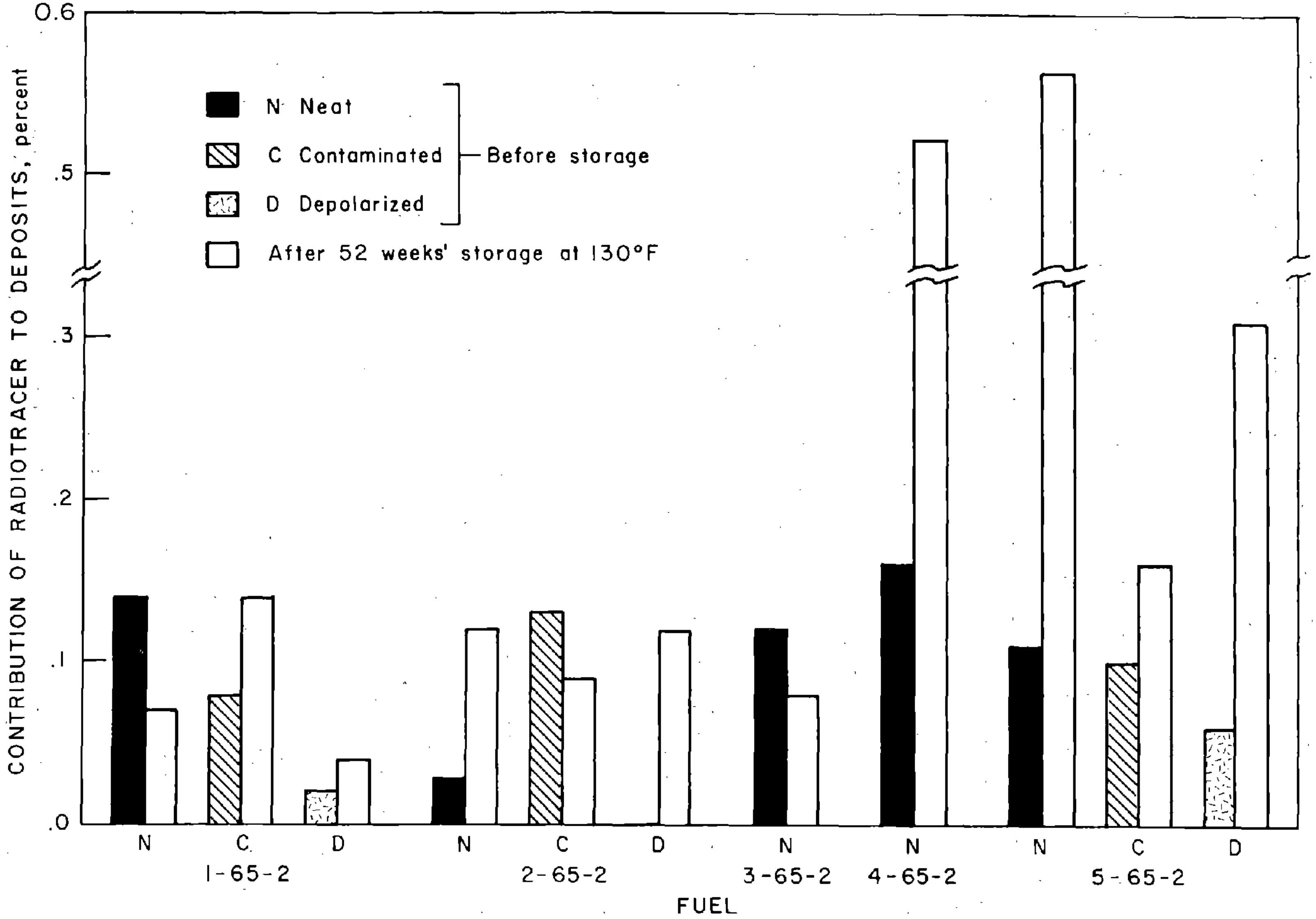


FIGURE 3. - Contribution of 1-Ethylindene-3-^{14}C to Total Deposits.

gum that deposited on the inside of the storage bottle, but recovery and measurement of these adherent deposits failed to account for any significant losses. Apparently a volatile component containing the radioactivity was formed during storage.

1-Methylindan-3-^{14}C

No significant deposit contribution was noted from the labeled 1-methylindan-3-^{14}C for the five blends tested before storage. After 52 weeks at elevated temperature, however, slight increases in contribution to total deposits were noted for three of these five blends. A fourth blend showed no effect from the storage; however, the fifth blend showed a very significant contribution from the labeled component. Results are summarized in table 4 and figure 4.

TABLE 4. - Storage stability of blends containing 1-methylindan-3-^{14}C, tetralin-^{14}C, 1,2,3,5-tetramethylbenzene-^{14}C, 1-methylindene-3-^{14}C, and n-hendecane-1-^{14}C

Fuel (neat)	Radiotracer	Contribution of radiotracer to total deposits, percent		Radioactivity recovery, percent
		Before storage	After 52 weeks at 130° F	
1-65-2	1-Methylindan-3-^{14}C...	0.012	0.088	100.8
2-65-2	..........do..........	.007	.055	99.3
3-65-2	..........do..........	.018	.057	99.9
4-65-2	..........do..........	.027	1.310	96.7
5-65-2	..........do..........	.062	.060	98.5
1-65-2	Tetralin-^{14}C..........	.038	.003	99.4
2-65-2	..........do..........	.061	.094	101.0
3-65-2	..........do..........	.001	.008	100.0
4-65-2	..........do..........	.033	.773	96.6
5-65-2	..........do..........	.037	.089	98.8
1-65-2	1,2,3,5-Tetramethyl-benzene-^{14}C..........	.010	.013	100.0
1-65-2	1-Methylindene-3-^{14}C..	.013	.019	98.8
2-65-2	..........do..........	.056	.105	99.6
3-65-2	..........do..........	.105	.169	99.5
4-65-2	..........do..........	.121	7.142	85.9
5-65-2	..........do..........	.111	.268	98.6
1-65-2	n-Hendecane-1-^{14}C.....	.033	.055	98.2
2-65-2	..........do..........	.029	.036	101.9
3-65-2	..........do..........	.060	.014	99.6
4-65-2	..........do..........	.202	.373	101.6
5-65-2	..........do..........	.143	.147	101.2

Tetralin-^{14}C and 1,2,3,5-Tetramethylbenzene-^{14}C

Results from tests of blends containing tetralin and a tetramethylbenzene as the labeled component are shown in table 4 and figures 5 and 6. The tetralin blends displayed the same general trend as the indan blends. Only one fuel

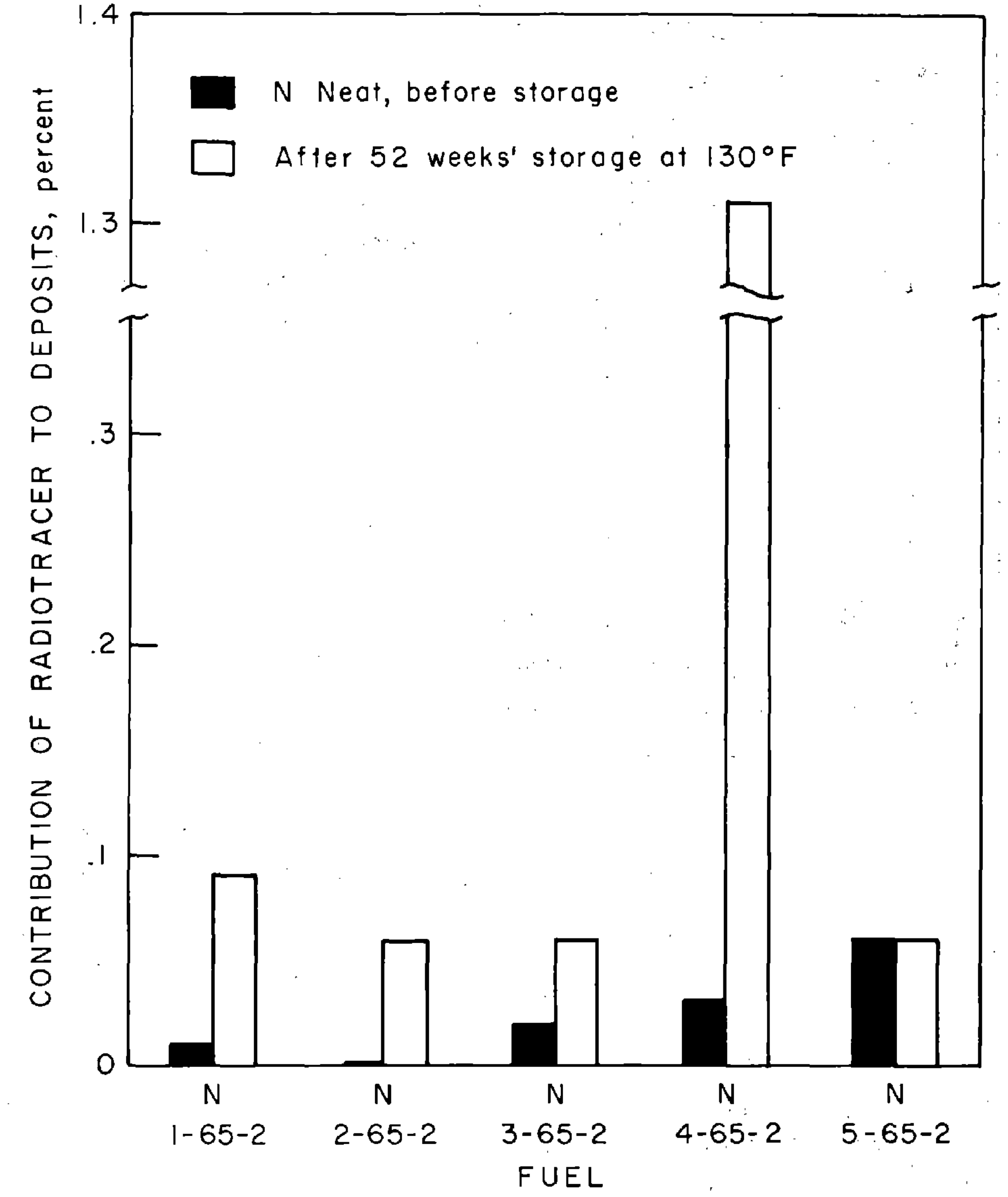


FIGURE 4. - Contribution of 1-Methylindan-3-^{14}C to Total Deposits.

showed a substantial increase of tracer participation in deposit-forming mechanisms during 52 weeks of storage. This was the same fuel that showed the largest change with the 1-methylindan, 1-methylindene, and also with 1-ethylindene previously discussed. The fuel is a JP-6 type, designated as 4-65-2. The tetramethylbenzene blend showed no significant tendency toward change during storage.

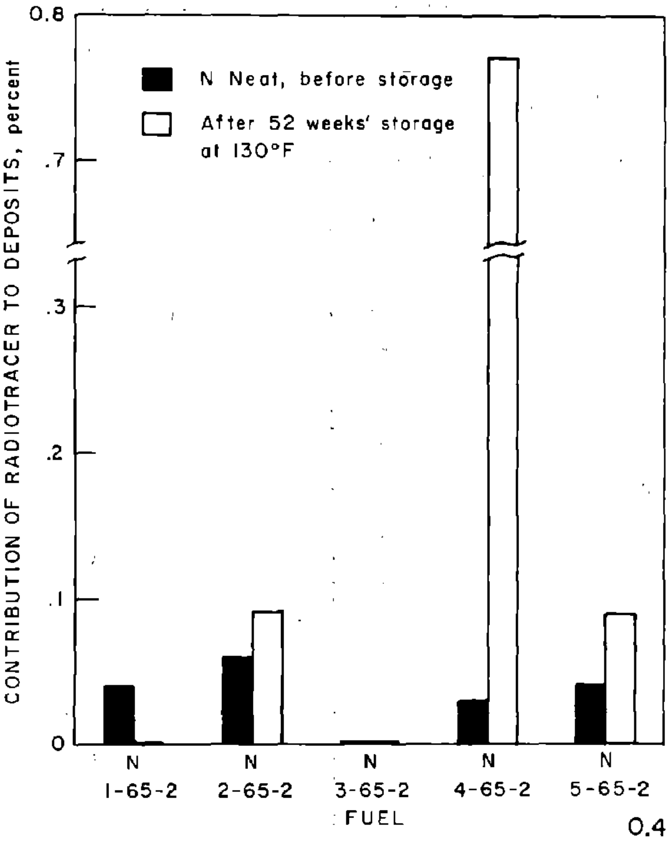
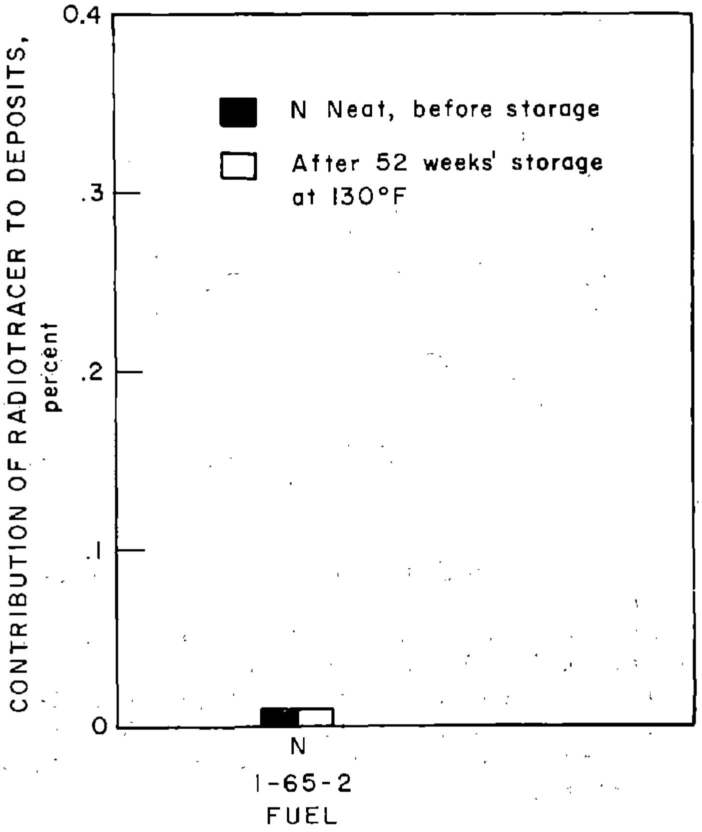


FIGURE 5. - Contribution of Tetralin-^{14}C to Total Deposits.

FIGURE 6. - Contribution of 1,2,3,5-Tetramethylbenzene-^{14}C to Total Deposits.



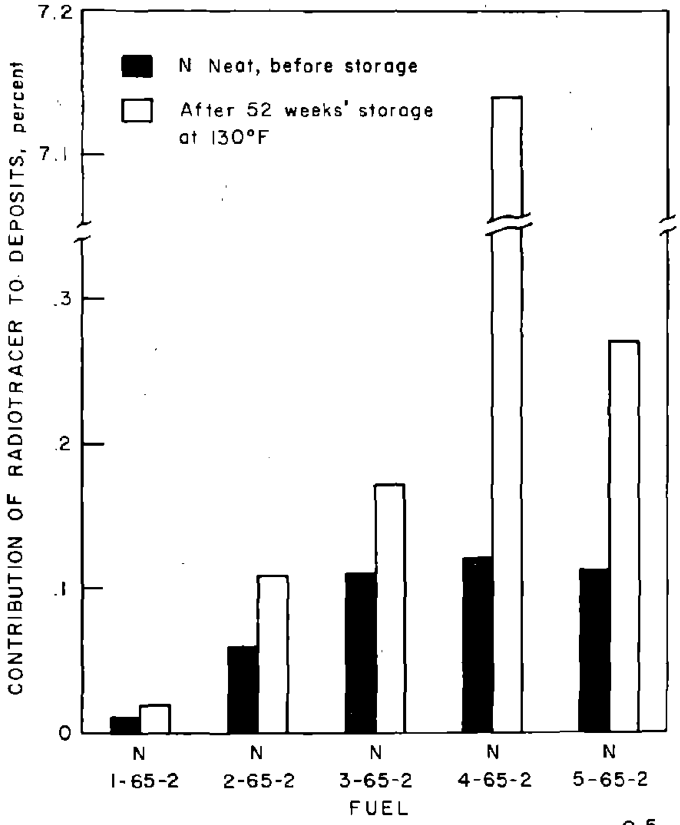


FIGURE 7. - Contribution of 1-Methylindene-3-^{14}C to Total Deposits.

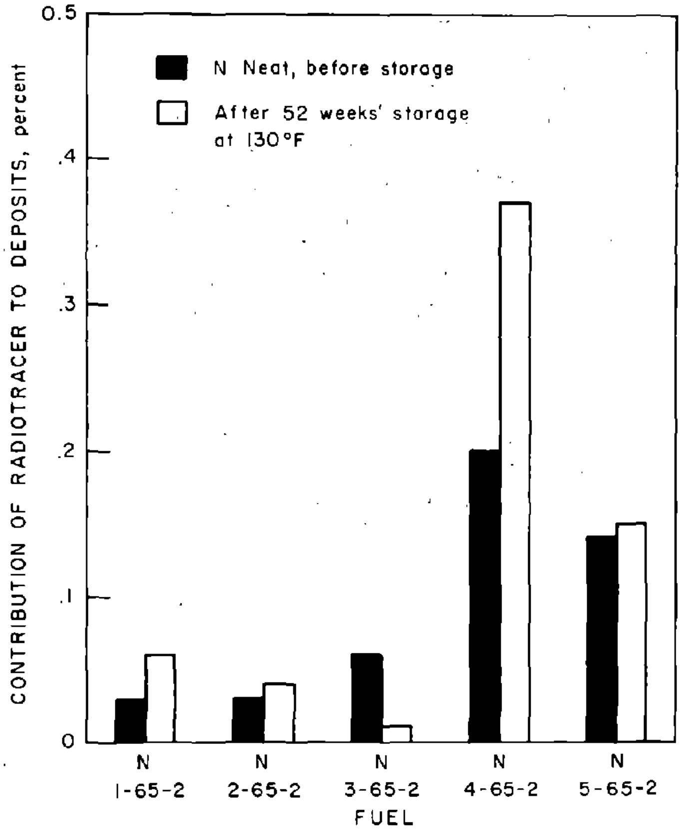


FIGURE 8. - Contribution of n-Hendecane-1-^{14}C to Total Deposits.

1-Methylindene-3-^{14}C

The data from five blends containing 1-methylindene-3-^{14}C (fig. 7 and table 4) showed an extraordinarily large contribution of the radiotracer to total deposits in fuel 4-65-2. The radioactivity balance was poor for this blend, and since radioactivity could not be found in the gum recovered from the interior walls of the storage bottle, it was concluded that this loss was associated with volatile reaction products containing carbon-14.

n-Hendecane-1-^{14}C

Five blends of n-hendecane-1-^{14}C in jet fuel were retested after 52 weeks of storage, and the data are plotted in figure 8 and included in table 4. As anticipated, the quantity of deposits after storage was similar to that before storage. Fuel 1-65-2 showed a slight increase in filterable deposits, and fuel 4-65-2 showed a somewhat larger increase, but these changes were small.

2-Methyl-^{14}C-Naphthalene

Data for 14 test blends containing 2-methyl-^{14}C-naphthalene as a radiotracer are plotted in figure 9. Each of these blends was tested, as before, for radiotracer contribution to deposits in the microfuel coker at the threshold failure temperature of the neat unstored fuel. Naphthalene types are known to be common fuel constituents of not only jet fuels, but also of motor gasolines. Earlier experimentation in the field of motor gasoline storage stability by the Bureau of Mines (5) led investigators to conclude that storage characteristics were often adversely affected by higher molecular-weight aromatic compounds, such as 2-methylnaphthalene. The present experiments were designed to determine the contribution of these compounds to deposits formed in jet fuels after storage. Data for these studies are summarized in table 5. The level of the carbon-14-labeled aromatic compound was held to 1 ppm or less in each blend to avoid a gross effect upon the thermal stability of the fuels. The principal finding from these tests was that 2-methylnaphthalene's contribution to total deposits was very low. Even after storage, 0.1 percent or less of the initial level of radiotracer was found in total deposits, which included deposits on the preheater tube and on the filter.

2,6-di-t-Butyl-^{14}C-p-Cresol

The test blends that contained the labeled antioxidant 2,6-di-t-butyl-^{14}C-p-cresol showed very little participation of the antioxidant in deposit-forming reactions, even after 52 weeks of storage at 130° F. The cresol blends are presented graphically in figure 10 and summarized in table 6.

TABLE 5. - Storage stability of blends containing 0.7 ppm of 2-methyl-^{14}C-naphthalene

Fuel	Treatment	Contribution of radiotracer to total deposits, percent		Radioactivity recovery, percent
		Before storage	After 52 weeks at 130° F	
1-65-2	Neat..................	0.031	0.096	99.7
	Contaminated..........	.020	.101	100.3
	Depolarized...........	.002	.025	98.8
2-65-2	Neat..................	.103	.033	99.2
	Contaminated..........	.056	.061	98.7
	Depolarized...........	.039	.038	100.4
3-65-2	Neat..................	.117	.029	100.2
	Contaminated..........	.070	.014	100.0
4-65-2	Neat..................	.087	.064	99.7
	Contaminated..........	.124	.122	99.8
	Depolarized...........	.088	.051	98.4
5-65-2	Neat..................	.166	.023	101.1
	Contaminated..........	.109	.031	99.3
	Depolarized...........	.049	.074	100.3

TABLE 6. - Storage stability of blends containing 8 ppm of 2,6-di-t-butyl-^{14}C-p-cresol

Fuel	Treatment	Contribution of radiotracer to total deposits, percent		Radioactivity recovery, percent
		Before storage	After 52 weeks at 130° F	
1-65-2	Neat..................	0.160	0.196	95.7
	Contaminated..........	.201	.261	99.5
	Depolarized...........	.000	.068	94.9
2-65-2	Neat..................	.038	.040	100.2
	Contaminated..........	.033	.036	98.7
	Depolarized...........	.037	.102	99.9
3-65-2	Neat..................	.044	.076	98.2
4-65-2	Neat..................	.078	.115	99.7
5-65-2	Neat..................	.107	.074	99.3
	Contaminated..........	.038	.085	98.0
	Depolarized...........	.048	.106	99.2

N,N'-di-sec-Butyl-4-^{14}C-p-Phenylenediamine

Test data for the 11 blends before and after storage that contained N,N'-di-sec-butyl-4-^{14}C-p-phenylenediamine, an amine-type antioxidant, are presented in figure 11. Table 7 shows the summary data. Very large amounts of radioactivity from the labeled additive were found in the deposits formed by thermal stress of the blends at the threshold failure temperature of the neat fuel. Apparently, from the data, the deposit-forming tendency of this compound depends greatly upon the fuel environment since the percentage of radiotracer that went into deposits ranged from 1 to 56 percent in the different fuels. The contribution of this amine-type radiotracer to deposits was apparently smaller after storage than before storage. This phenomenon was most noticeable in the blends with 1-65-2, a JP-5 fuel. Many of the blends also showed very poor radioactive material balances. Loss of radioactivity occurred during both the initial and final microfuel coker thermal-stability tests. In addition, those blends with fuel 1-65-2 showed a large loss of radioactivity during storage, and blends of fuel 5-65-2 showed a smaller but significant loss of radioactivity during storage. The poorest radioactivity balance was exhibited by the blend of depolarized fuel 1-65-2; approximately 40 percent of the initial radioactivity was lost during storage, and another 40 percent was lost in the final thermal-stability tests. Very little radiotracer could be recovered from the storage bottle. The butyl group, which contains the radioactive carbon-14 atom, apparently fragmented from the parent molecule and was lost through volatility. This fragmentation and loss of radioactivity was observed in previous studies (<u>10</u>) performed with a static thermal-stability test apparatus. In that earlier work, the off-gas from the test apparatus was checked at the end of the heating period of a blend containing di-t-butyl-^{14}C-p-cresol in a turbine aircraft fuel. Gas chromatographic separation of the gaseous products of the thermal-stability test, followed by mass spectrometric analysis, identified three radioactive species. The largest was isobutene, followed in quantity by isobutane and n-butane. The indication from that study was a fragmentation of the butyl group from the cresol molecule with subsequent volatilization and loss of species derived from this butyl group. Depending on the fuel environment, this thermal degradation of the antioxidant can apparently occur, to some extent, at the relatively low temperature of storage as well as at the high temperature of the thermal-stability test.

TABLE 7. - Storage stability of blends containing N,N'-di-sec-butyl-4-^{14}C-p-phenylenediamine

Fuel	Treatment	Radiotracer conc., ppm	Contribution of radiotracer to total deposits, percent		Radioactivity recovery, percent
			Before storage	After 52 weeks at 130° F	
1-65-2	Neat.........	5	40.06	16.60	[1]56.8
	Contaminated.	2	42.47	16.92	[1]59.5
	Depolarized..	3	35.04	0.92	[2]17.3
2-65-2	Neat.........	2.5	2.20	1.60	90.5
	Contaminated.	2.5	1.21	1.79	92.7
	Depolarized..	2.5	7.16	6.64	73.2
3-65-2	Neat.........	3	10.49	4.68	77.1
4-65-2	Neat.........	2.5	17.99	21.43	62.3
5-65-2	Neat.........	3	49.88	44.15	[3]70.9
	Contaminated.	3	53.03	56.75	[3]80.8
	Depolarized..	2.5	15.11	6.60	[3]65.4

[1] Approximately one-fourth of the loss of radioactivity occurred during storage.

[2] One-half of the loss occurred during storage.

[3] Approximately one-tenth of the loss occurred during storage.

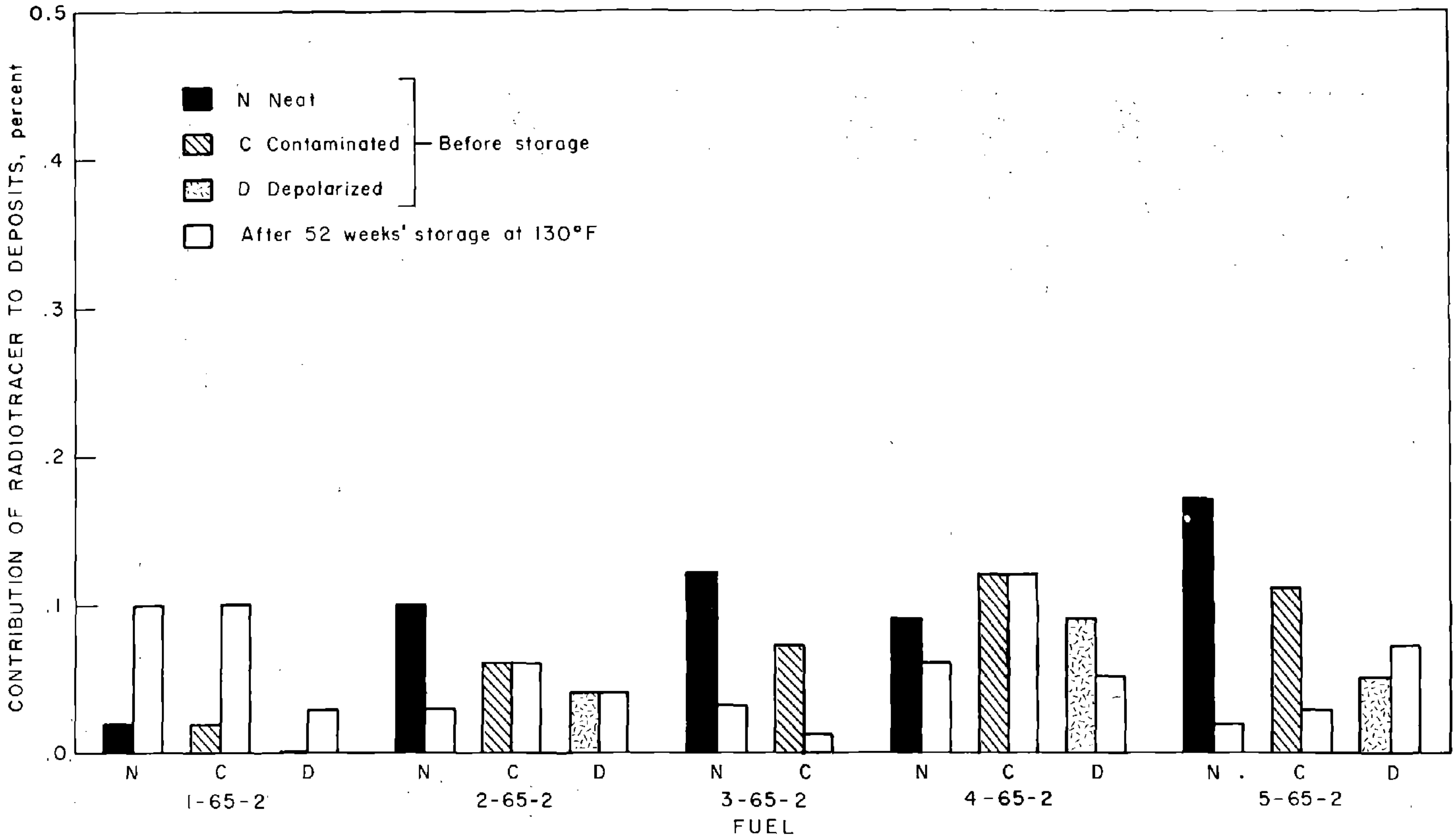


FIGURE 9. - Contribution of 2-Methyl-^{14}C-Naphthalene to Total Deposits.

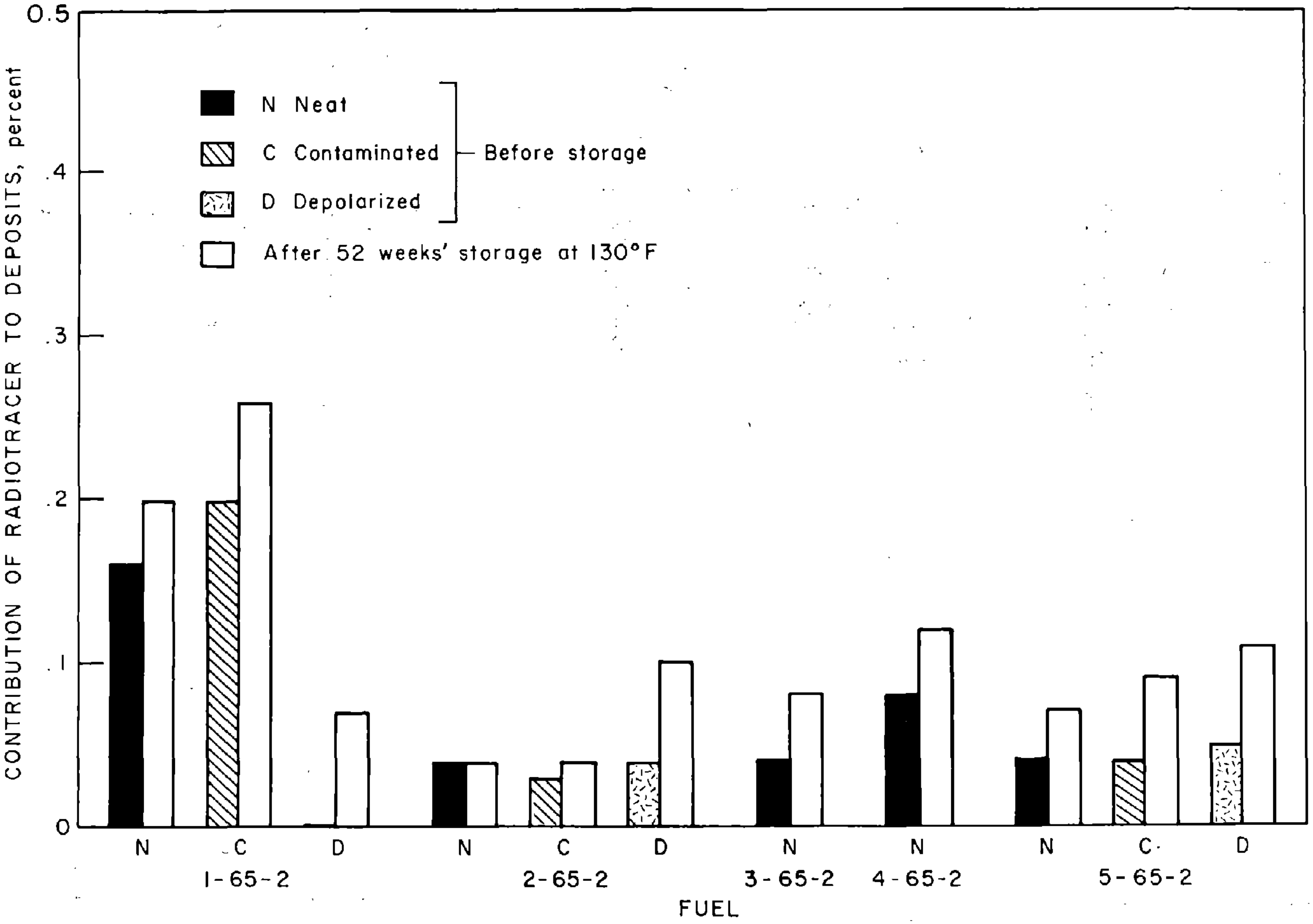


FIGURE 10. - Contribution of 2,6-di-t-Butyl-^{14}C-p-Cresol to Total Deposits.

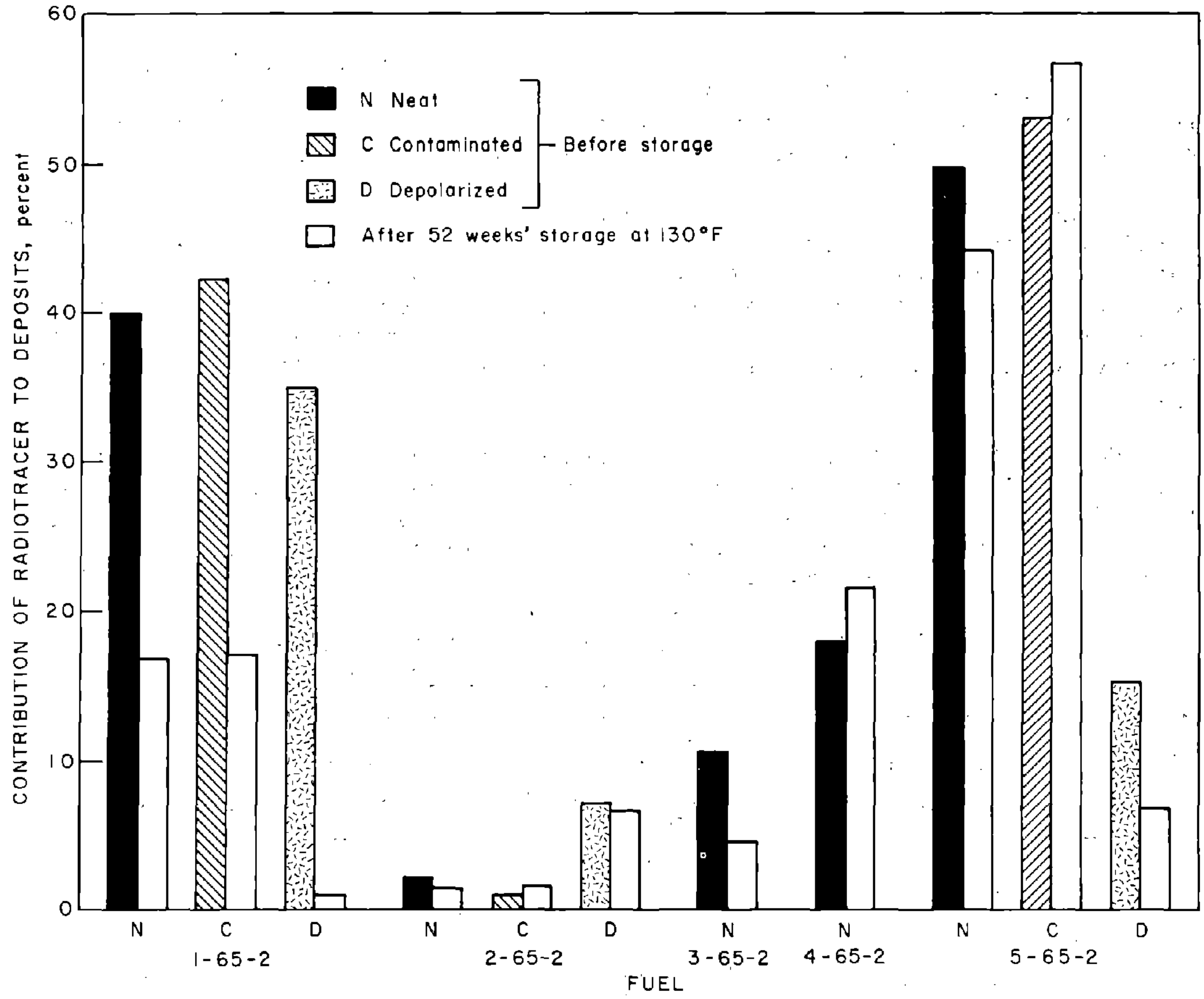


FIGURE 11. - Contribution of N,N'-di-sec-Butyl-4-^{14}C-p-Phenylenediamine to Total Deposits.

Contamination of the fuel with red iron oxide (Fe_2O_3) and water barely affected the reaction and fragmentation of this labeled antioxidant. Results from test fuel 1-65-2 (neat) and 1-65-2 (contaminated) were similar, as were those of pairs 2-65-2 (neat) and 2-65-2 (contaminated) and fuel 5-65-2, both neat and contaminated.

Depolarization was less consistent in its total effect. Depolarized blends with fuels 1-65-2 and 2-65-2 consumed more antioxidant during storage and testing than did the neat fuel blends; this indicated a less stable environment after depolarization. Another blend, with depolarized fuel 5-65-2, contributed less antioxidant to deposits formed in the thermal-stability test than did the neat fuel; this indicated an improvement in fuel quality as a result of depolarization.

Oleic-1-^{14}C Acid

Discussions with other investigators disclosed possible deleterious effects of trace quantities of oleic acid in jet fuels. Extensive deposit formation and filter plugging reportedly results from an interaction between the oleic acid and the cadmium parts of fuel tanks and plumbing systems.

Blends that contained 250 ppm oleic acid labeled with carbon-14 were prepared with each of the five test fuels and tested in the microfuel coker before and after storage for 52 weeks at 130° F. One blend with each fuel consisted of the neat fuel and the oleic acid; a second blend was identical except that three cadmium-plated screws were placed in the bottle to simulate the environment that apparently produces troublesome deposits in aircraft fuel systems.

Fuels 3-65-2, 4-65-2, and 5-65-2 showed some initial contribution of the oleic-^{14}C acid to total deposits, as shown in figure 12 and table 8. Since the cadmium screws were in contact with the fuel only 24 hours at room temperature, it is believed that the initial reaction of oleic acid was due to the fuel environment rather than the cadmium.

TABLE 8. - Storage stability of blends containing 250 ppm of oleic-1-^{14}C acid

Fuel	Treatment	Contribution of radiotracer to total deposits, percent		Radioactivity recovery, percent
		Before storage	After 52 weeks at 130° F	
1-65-2	Neat..................	0.004	0.339	96.8
1-65-2	With cadmium..........	.001	1.681	[1]92.0
2-65-2	Neat..................	.002	.258	[1]91.5
2-65-2	With cadmium..........	.116	1.184	88.9
3-65-2	Neat..................	.529	.341	[1]91.0
3-65-2	With cadmium..........	.414	.982	90.9
4-65-2	Neat..................	.433	2.218	[1]90.5
4-65-2	With cadmium..........	.527	2.721	[1]88.8
5-65-2	Neat..................	.679	.312	[1]92.8
5-65-2	With cadmium..........	.885	1.284	[1]88.9

[1] About half of the loss of radioactivity occurred during storage.

When tested after storage, all five blends which had been stored in contact with cadmium showed a significantly greater contribution of oleic-^{14}C acid to total deposits than did the neat fuel blends. The blend of fuel 4-65-2, without cadmium, showed a large increase in deposits as a result of storage, but the blend with cadmium produced an even larger increase. These results indicated that oleic acid in a fuel does indeed interact with the cadmium to produce deleterious effects on the thermal-stability quality of fuel stored in contact with cadmium.

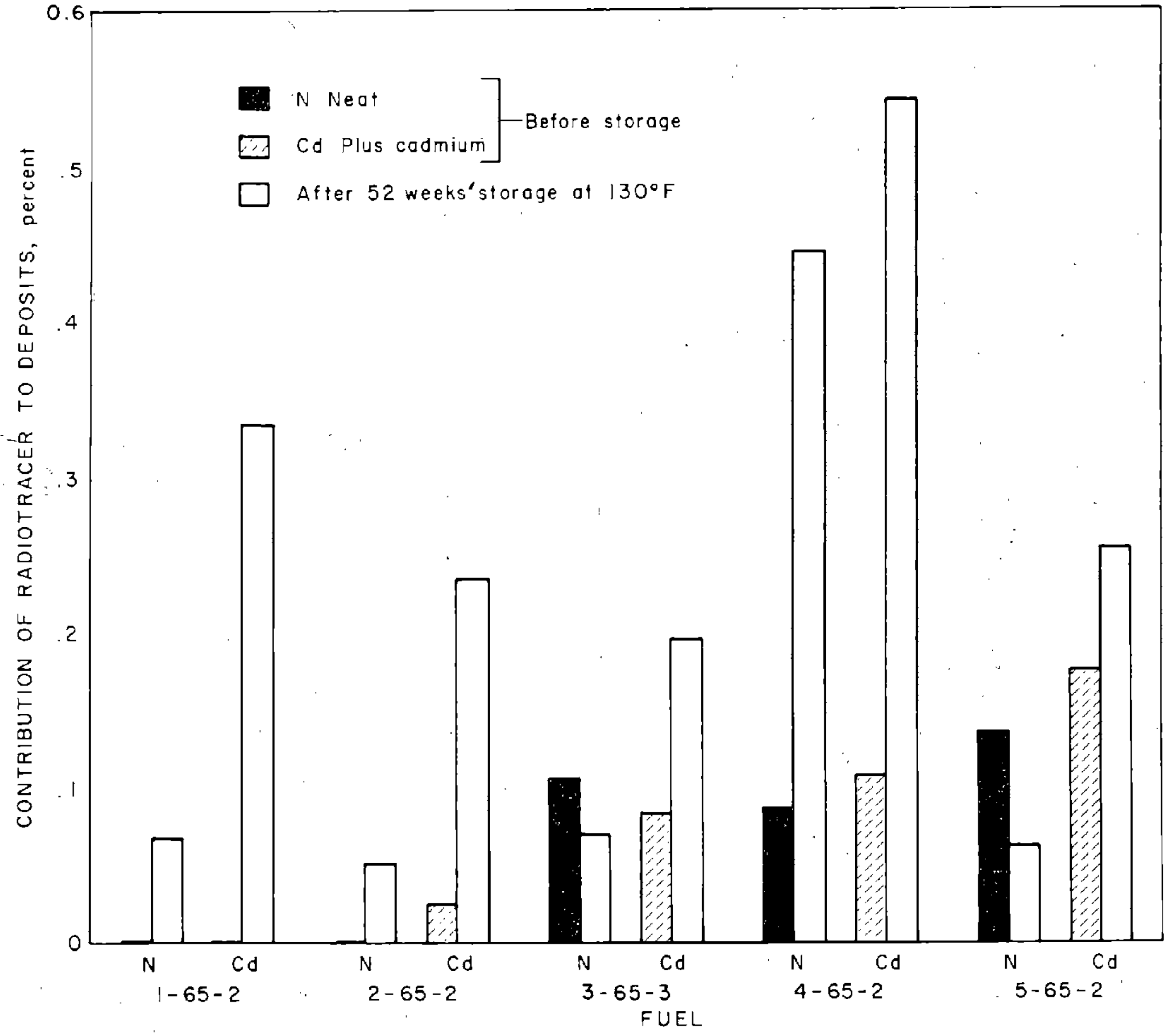


FIGURE 12. - Contribution of Oleic-1-^{14}C Acid to Total Deposits in Presence of Cadmium.

1,5-Hexadiene-1,6-^{14}C

Owing to a limited amount of the labeled compound 1,5-hexadiene-1,6-^{14}C, only two blends were prepared. Table 9 and figure 13 show that about 0.2 percent of the initial radiotracer was found in the deposits formed in the initial microfuel coker test, and about double that amount was found in the deposits from the final test.

The radioactivity balance was poor, with a significant part of the loss of radioactivity having occurred during the 52 weeks of storage. This loss can probably be attributed to volatility and/or fragmentation of the hexadiene.

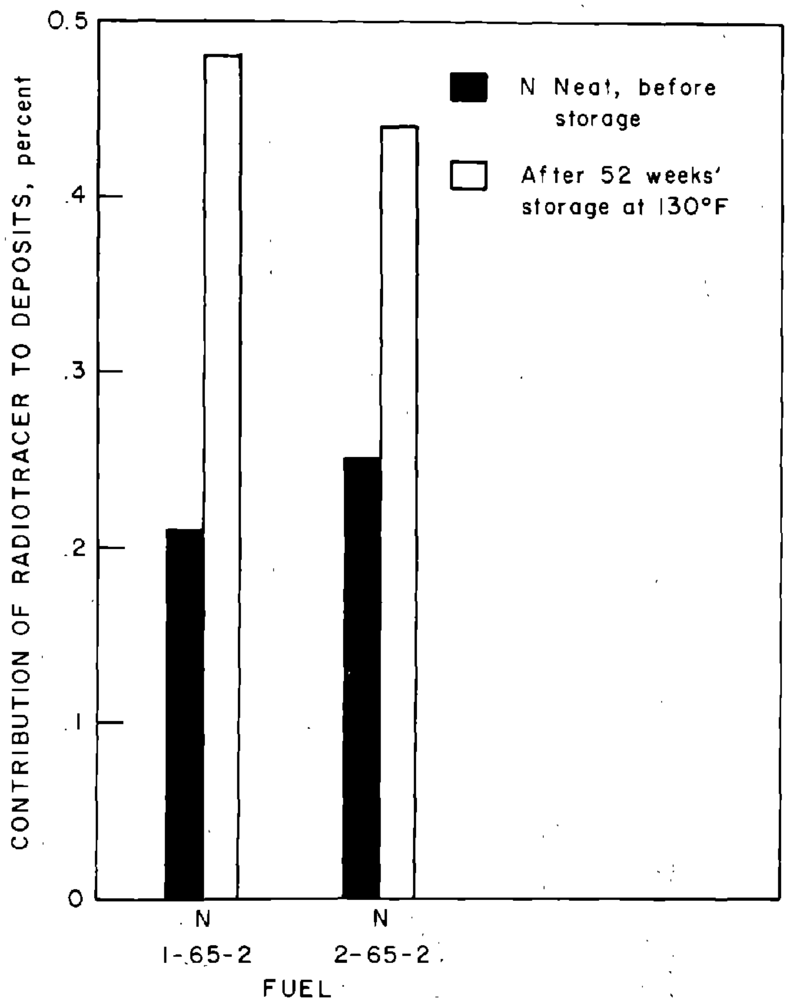


FIGURE 13. - Contribution of 1,5-Hexadiene-1,6-^{14}C to Total Deposits.

TABLE 9. - Storage stability of blends containing 2 ppm of 1,5-hexadiene-1,6-^{14}C

Fuel (neat)	Contribution of radiotracer to total deposits, percent		Radioactivity recovery, percent[1]
	Before storage	After 52 weeks at 130° F	
1-65-2	0.214	0.484	39.7
2-65-2	.253	.438	50.1

[1] About one-third of the loss of radioactivity occurred during storage.

N,N'-Disalicylidene-1,2-Diaminopropane

Five blends, one with each of the five test fuels, were prepared with a carbon-14-labeled metal deactivator N,N'-disalicylidene-1,2-diaminopropane as the radiotracer. The concentration of metal deactivator in each blend was approximately 10 ppm. The storage period was for only 26 weeks.

With the exception of the least stable fuel blend, fuel 4-65-2 (JP-6), the results of the thermal-stability tests after storage were similar to the results before storage--from 1 to 20 percent of the carbon-14 was recovered in filterable deposits, and a small amount of the radioactivity was lost by fragmentation and volatilization during the coker test. The blend with fuel 4-65-2 behaved differently; more than 50 percent of the original radioactivity was lost during the final thermal-stability test in the microfuel coker. The filterable deposits collected after storage amounted to 19 percent of the radioactivity that remained after storage, compared with 5 percent filterable deposits before storage.

Excessive loss of radioactivity from the blend with fuel 4-65-2 was investigated, and 22 percent of the original radioactivity was found deposited on the inside of the storage bottle. The other 30 percent lost in storage apparently resulted from fragmentation of the molecule with volatilization of the fragment that contained the carbon-14. Table 10 summarizes and figure 14 illustrates the data for N,N'-disalicylidene-1,2-diaminopropane.

TABLE 10. - Storage stability of blends containing 10 ppm of N,N'-disalicylidene-1,2-diaminopropane-1-^{14}C

Fuel (neat)	Contribution of radiotracer to total deposits, percent		Radioactivity recovery, percent
	Before storage	After 26 weeks at 130° F	
1-65-2	7.71	13.40	98.3
2-65-2	2.11	0.79	[1]87.2
3-65-2	3.46	1.95	93.1
4-65-2	5.55	19.42	[2]30.0
5-65-2	20.26	21.14	86.1

[1] One-half of the loss of radioactivity occurred during storage.

[2] Approximately three-fourths of the loss of radioactivity occurred during storage.

Dilinoleic Acid-^{14}C

Dilinoleic acid, the active ingredient of a corrosion inhibitor, was also investigated in this project, and the resulting data are listed in table 11 and shown in figure 15. A small quantity of dilinoleic acid labeled with carbon-14 was obtained from a commercial supplier. The dilinoleic-^{14}C acid, as received, was diluted with the commercial corrosion inhibitor, and the resulting solution was blended with each of the five test fuels in the proper quantities to produce final blends that contained the equivalent of 20 pounds of active ingredient in 1,000 barrels of fuel.

TABLE 11. - Storage stability of blends containing dilinoleic acid-^{14}C

Fuel (neat)	Contribution of radiotracer to total deposits, percent		Radioactivity recovery, percent[1]
	Before storage	After 24 weeks at 130° F	
1-65-2	1.050	1.288	76.9
2-65-2	1.141	2.316	74.5
3-65-2	.666	1.163	71.5
4-65-2	.526	1.198	81.1
5-65-2	1.074	3.756	69.9

[1] About one-half of the loss of radioactivity occurred during storage.

Initial microfuel coker tests were performed on the blends, and aliquots of each blend were also stored at 130° F. However, the carbon-14-labeled dilinoleic acid was received so late in the 3-year program that the blends could be stored for only 24 weeks instead of the usual 52 weeks. All five of these blends showed some deterioration during storage, as evidenced by radioactivity associated with filterable deposits and the visual ratings of the preheater tubes. Between 10 and 20 percent of the total radioactivity of each blend was lost during storage, apparently through fragmentation and volatilization of the additive, since no radioactive deposits could be recovered from the storage bottles.

Radioactive material balances disclosed that another 12 to 16 percent of the labeled corrosion inhibitor was lost during the thermal-stability test in the coker. These tests indicated that the corrosion inhibitor contributed to loss of thermal-stability quality during storage and showed some contribution to preheater and filterable deposits during thermal stress both before and after storage.

Nonradioactive Blends

As a result of the findings from the use of trace amounts of carbon-14-labeled components to study jet fuel thermal stability, Bureau scientists decided to extend these investigations by storing some blends containing a similar nonradioactive component at a higher concentration level. The radiotracer levels were purposely held low, usually less than 20 ppm, to avoid changes in fuel characteristics. However, knowledge of the effect of larger than trace quantities of some fuel components, such as aromatic compounds, was needed.

Sixteen blends of the five test fuels with nonradioactive components were prepared as part of a special study. Six of these blends contained 1 percent of selected aromatic compounds, five blends contained an anti-icing additive, and five blends contained an organic sulfur compound. Results

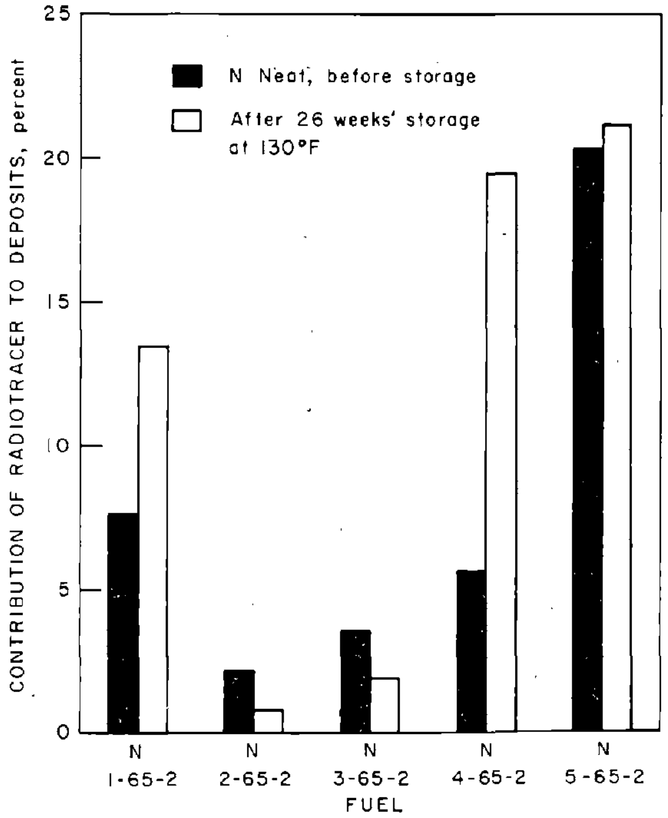
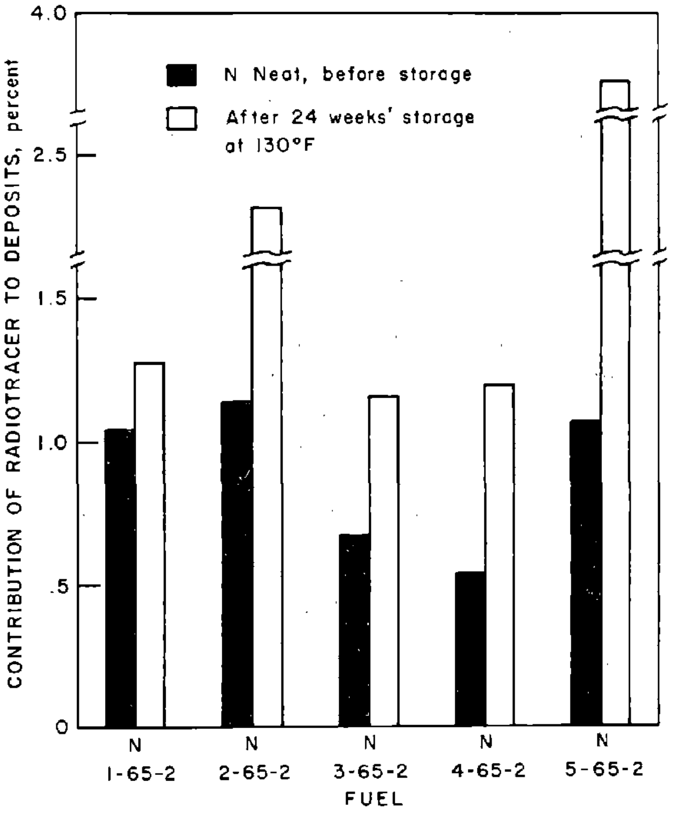


FIGURE 14. - Contribution of N,N'-Disalicylidene-1,2-Diaminopropane-1-^{14}C to Total Deposits.

FIGURE 15. - Contribution of Dilinoleic Acid-^{14}C to Total Deposits.



showed changes in thermal-stability quality of many of the blends containing sulfur compounds and aromatic hydrocarbons. The results of the microfuel coker tests, before and after storage, of these nonradioactive blends are listed in table 12.

TABLE 12. - Thermal stability of nonradioactive blends

Added component	Fuel No. and treatment	Test temperature, ° F, tube/fuel-out	Tube deposit rating		Length of storage at 130° F, weeks
			Before storage	After storage	
2-Methylnaphthalene (1 weight-percent).	1-65-2 neat.	480/290	2	1	52
1-Methyl-1-indene (1 weight-percent).	4-65-2 neat.	575/338	4	8	52
	5-65-2 neat.	725/412	5	8	52
1-Ethyl-1-indene (1 weight-percent).	4-65-2 neat.	575/338	2	4	46
	5-65-2 depolarized.	725/412	8	8	40
1-Ethylindan (1 weight-percent).	5-65-2 depolarized.	725/412	5	8	37
2-Methoxyethanol (0.1 volume-percent).	1-65-2 neat.	480/290	1	1	26
	2-65-2 neat.	625/362	5	5	26
	3-65-2 neat.	675/388	2	4	26
	4-65-2 neat.	575/338	2	1	26
	5-65-2 neat.	725/412	3	4	26
n-Butyl sulfide (0.3 volume-percent).	1-65-2 neat.	480/290	1	2	24
	2-65-2 neat.	625/362	4	5	24
	3-65-2 neat.	675/388	2	3	24
	4-65-2 neat.	575/338	2	7	24
	5-65-2 neat.	725/412	2	3	24

CONCLUSIONS

Hydrocarbon Fuel Components

Reactions in labeled hydrocarbon fuel systems, exclusive of the fuel additives, were greatest in blends containing 1-methylindene-3-^{14}C and 1-ethylindene-3-^{14}C. Next in order of magnitude were 1-methylindan-3-^{14}C and 1-ethylindan-3-^{14}C. Some reaction was also found in one blend of tetralin-^{14}C. The largest reaction of labeled fuel component was always in fuel 4-65-2, which is a JP-6 type with a failure temperature of 575° F. Even the paraffinic radiotracer hendecane showed some contribution to deposits in this fuel; however, 2-methylnaphthalene showed no reaction in any test fuel. From these findings it can be concluded that the JP-6 fuel represented the most unstable environment for the labeled fuel components previously listed, and that 1-ethylindene was the most reactive of the aromatic fuel components tested. It also can be concluded that although indenes and indans have been found in greater natural abundance in unstable jet fuels than in other stable fuels, they are not solely responsible for thermal instability in all systems and, in fact, are quite unreactive in some fuels. When stored without added radiotracers, no fuel showed a significant change in thermal-stability quality after 52 weeks at 130° F. Also, none of the five fuels displayed any quality changes as a result of contamination, depolarization treatment, and storage.

Fuel Additives

The greatest extent of reaction observed in the labeled fuel blends studied during the 3-year program was in those blends that contained the carbon-14-labeled antioxidant N,N'-di-sec-butyl-4-^{14}C-p-phenylenediamine. The amount of reaction or decomposition which formed filterable deposits varied greatly from fuel to fuel, with as much as 56 percent of the radiotracer recovered as filterable deposit from one fuel and only 1 percent filterable deposit in another fuel. Radioactivity losses, which were large for these blends, both during storage and in the thermal-stability tests, indicated fragmentation of the butyl group from the additive to yield a volatile product, which was lost through vaporization.

The second greatest amount of reaction was observed with another labeled amine-type additive, N,N'-disalicylidene-1,2-diaminopropane-1-^{14}C. The amount of radiotracer recovered as filterable deposits ranged from 1 to 20 percent. Again, some radiotracer was lost through fragmentation and vaporization of the volatile product, with fuel 4-65-2 showing the greatest loss.

Oleic-^{14}C acid blended with a jet fuel was found to interact with cadmium during storage to form more filterable deposits than were formed when the blend was stored without cadmium.

There was a slight amount of reaction during storage in blends that contained a corrosion inhibitor, dilinoleic-^{14}C acid, and some loss of radioactivity. The greatest reaction with dilinoleic-^{14}C acid was in fuel 5-65-2, which had the highest threshold failure temperature of all fuels studied.

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