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DETERMINATION OF THE HYDROPEROXIDE POTENTIAL OF JET FUELS

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DETERMINATION OF THE HYDROPEROXIDE POTENTIAL OF JET FUELS

Prepared by the

Hydroperoxide Potential of Jet Fuels Panel

of the

CRC Oxidation Stability of Gas Turbine Fuels Group

April 1988

Aviation Vehicle Fuel, Lubricant, and Equipment Research Committee

of the

Coordinating Research Council, Inc.

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APPENDICES

I. SUMMARY

In 1963 and in 1976, peroxide attack on certain engine rubber parts was found on some Far Eastern fuels. The problem was corrected by requiring oxidation inhibitor be added to fuels meeting Specifications DERD 2494 and MIL-T-5624. Because the majority of commercial aviation turbine fuel had not shown significant peroxide formation, CRC was requested to develop a technique which would identify the hydroperoxide-forming tendencies of jet fuels. Heating the fuel at 65°C for four weeks and measuring the peroxide number after four weeks is concluded to be an adequate Go/No Go test. Keywords: Gas turbine turbine components. (A.W.

II. INTRODUCTION

The first instances of rubber attack by peroxides were found by the British in the Far East in 1962. Both neoprene and nitrile rubber components hardened in high temperature regions and split on subsequent flexing. Failures occurred after a few hundred hours instead of the normal 8,000 hours. Heating fuel at 100°C in the presence of rubber and measuring peroxide content identified the problem fuels. It was concluded that hydrogen treating had removed natural antioxidants, leading to the formation of peroxides during fuel storage. Either the addition of antioxidants or blending the fuel with non-hydrotreated stocks prevented the problem. Rather than try to identify and correct individual potential problem fuels, Specification DERD 2494 was changed to require the addition of approved oxidation inhibitors to all hydrotreated stocks.

Because the problem had not occured on hydrotreated fuels made in other parts of the world, there was reason to believe that the type or severity of hydrotreating played a major role. It was considered likely that mild, low-pressure hydrotreating (sometimes called "hydrosweetening") did not destroy the natural antioxidants while severe, high-pressure hydrotreating might. Because the bulk of the world's jet fuel was not severely hydrotreated and no rubber problems had occurred, other specifications were not changed at that time.

In Spring 1976, the US Navy found cracking of rubber fuel control diaphragms when engines were operated on certain Japanese JP-5 fuels. Specification MIL-T-5624K was amended in November 1976 to require the addition of oxidation inhibitors to all JP-5 fuels and to JP-4 fuels containing hydrotreated blending stocks. This action seems to have prevented further such problems in US military fuels. Interestingly, the Royal Thai Air Force reported elastomer problems in 1984 with uninhibited JP-4. Reportedly, these problems disappeared after additive addition and a change in elastomers.

Although the additive inclusion prevented further performance problems, inhibitor shortages in 1974 and later created supply difficulties and highlighted the need for a procedure which would identify peroxide-forming problem fuels. As a result, the CRC Group on Oxidation Stability of Jet Fuels agreed in 1980 to form the Hydroperoxide Potential of Jet Fuels Panel to develop such a procedure. Panel membership and participants in the three round robin programs are shown in Appendix A.

III. TEST METHOD DEVELOPMENT

A. Initial US Navy Tests

Initial test development was carried out by the Naval Research Laboratory who tested one Jet A and a number of JP-5 fuels at 100°C, measuring hydroperoxide content by ASTM D1563. A more detailed summary of this work is given in Appendix B. Based on other work*, a maximum of 1 milliequivalent per kilogram (meq/kg) was considered an acceptable level of hydroperoxide formation. The Laboratory concluded that the test gave reasonable repeatability, distinguished between different samples and noted that antioxidants inhibited the peroxidation of petroleum-derived fuels, but not that of shale-derived fuels.

B. Cooperative Test Programs 1 and 2

The first test program consisted of testing duplicate samples of seven fuels at 100°C in six laboratories. Fuel peroxide levels were checked by ASTM D3707 after 3, 7, 24, 48, 72, 96, and 168 hours. Fuels included a severely hydrotreated JP-5 with and without antioxidant; JP-4 without antioxidant; a moderately treated Jet A without antioxidant; and a severely hydrotreated, uninhibited JP-5 made from oil shale. ASTM D3707 was modified to use 1,1,2-trichloro-1,2,2-trifluoroethane (Freon 113) instead of carbon tetrachloride. Test results are contained in Appendix C. Again, the agreement between

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* R. H. Shertzer, "Aircraft Systems Fleet Support/Organic Peroxides in JP-5 Investigation," Final Report NAPC-LR-78-20, Naval Air Propulsion Center, Trenton, NJ, September 27, 1978.

duplicate samples at the same laboratory was acceptable but large differences were noted between laboratories on specific fuels. It was also found that antioxidants delayed but did not inhibit peroxide formation in two heavily hydrotreated fuels at this test temperature. These findings encouraged the Panel to consider lower test temperatures and to closely review test apparatus and possible other differences between laboratories.

To establish the temperature effect, the Naval Researach Laboratory tested four fuels from the first program at 43, 65, and 80°C. The results are detailed in Appendix D, but data analysis indicated that for at least two of the fuels the results at lower temperatures could not be related to results obtained at 80 and 100°C. High temperature results therefore may be unable to predict peroxide formation at normal storage temperatures and another program was proposed to run at 65°C for ten weeks.

The second cooperative program included a severely treated JP-5 with and without oxidation inhibitor; a severely treated, shale-derived inhibited JP-4; a petroleum-derived JP-4; and a moderately treated JP-5, all to be stressed at 65°C ± 1°C. In this program, samples were purged with and shipped under nitrogen. Six laboratories participated and samples were run in duplicate as before. A sample of a stable hydroperoxide was circulated to check possible analytical error. All ovens were calibrated. Program instructions for the second cooperative test program are included in Appendix E. The results of the second program will be found in Appendix F. Unfortunately, it had not been possible to obtain all the desired fuels with the result that four of the five fuels contained oxidation inhibitor and did not form high levels of hydroperoxide after fifty-six days. The fuel which formed high levels of peroxide again showed high laboratory-to-laboratory variability with more consistent results within laboratories. It was therefore decided that the 65°C test would not serve as a quantitative predictor of peroxide levels but could serve as a go/no-go test to identify fuels with high peroxide-forming potential. A third program, however, with more fuels was considered desirable to more firmly establish the test's potential.

A useful portion of the second program was the testing and analysis of the stable hydroperoxide sample to establish the effect of the analytical method on data variability. Here it was found that the with-in laboratory spreads (the immediate repeatability based on two sets of quadruplicates) for the calibration standard varied from 0.2 to 15.4 percent, with an average value of 6.2 percent. The corresponding pooled standard deviation and repeatability values were 3.5 and 9.8 percent, respectively. The laboratory averages for peroxide number (reproducibility) varied from 9.20 to 10.51 meq/kg, giving a spread of 13 percent. The corresponding standard deviation was 14.6 percent and the repeatability was 41 percent. These relatively low values indicated that the analytical method contributed only a minor component to the variability of the accelerated test results.

C. Cooperative Test Program 3

1. Experimental Work

The third test program was planned to enlarge on the previous programs and to ensure that a majority of the sample fuels would develop significant levels of peroxides (more than 1 meq/kg). For the latter goal, fuels were selected carefully from a broader range of sources and it was stipulated that they had to have been hydrotreated and contain no anti-oxidant. Samples chosen included JP-5's, Jet A's, blending stocks and a shale JP-4. These are identified in Table I. Ten or fifty gallons of each fuel were obtained and 2/3 gallon each was supplied to the laboratories. Each fuel was stated by the supplier to contain no anti-oxidant. Fuels #5 and #8 were labelled as having no additives. Fuel samples were shipped under argon but were to be aerated before putting in the oven. The plan called for nine fuels and eight laboratories, as compared to the 5x6 matrix in the second round robin, and three sample bottles of each fuel instead of two. This was to permit improved statistical conclusions. The instructions called for putting 400 ml samples in each bottle so that at least 50 ml could be taken at each sampling time. Note that only one analysis per bottle was made at each time. One analysis on each of three identical samples (bottles) at each time is more useful than triplicate analyses on one bottle.

Thus, each laboratory set up twenty-seven samples instead of ten in Round Robin 2, but the number of sampling times was six instead of eight. It was intended originally to limit the time at 65°C to two or three weeks. However, screening tests at NRL indicated that a longer time was needed in order to develop more peroxides. Thus, the time was extended to six weeks with analyses at 0, 7, 14, 21, 28 and 42 days. Greater access of samples to atmospheric oxygen while in the oven was provided in this program. A calibration sample, as described above for the previous program, was furnished again to check the variability due to the analytical method alone (and also biases between laboratories). The hydroperoxide level this time was approximately 3 instead of 10 meq/kg. Instructions and notes on procedure were distributed to participants in a letter dated April 7, 1986 (shown in Appendix G).

2. Analysis of Results

Detailed analytical results of the accelerated test program are included in Appendix H. The averages are graphed in Figures 1 through 9. These results should be studied in comparison with the results of the second round robin, which are shown in Appendix C. Note that Texaco conducted duplicate rather than triplicate bottle tests and duPont omitted analysis at three weeks. It is apparent that appreciable variation exists between bottles and between laboratories. Development of hydroperoxides in fuels involves free radical reactions among hundreds of compounds and appears to be inherently variable.

The components of variability are discussed in the following sections. These include variability of the analytical method, variability between triplicate fuel samples within one laboratory, and variability between laboratories. In spite of such variability it appears, on careful examination of the results, that the 65°C test can distinguish between stable and unstable fuels in about three weeks (see 2-f below).

a. Analytical Variability

The non-stressed control sample (see 2-d below) provided the primary data on variability attributable to the iodometric analytical method. Additional information was obtained from duplicate fuel analyses. Such duplicate results (same bottle, same day) were reported by Texaco, NIPER, and Exxon. (Repeat analyses had been requested whenever a set of triplicate bottles varied by more than 15 percent or 0.3 meq/kg in the case of results below 1 meq/kg). The close agreement of these 76 pairs of data supports strongly the conclusion that the differences between bottles (see below) are real. An analysis of the data is as follows:

Range of differences between duplicates[a]	0-40%
Average difference	5.0%
Pooled standard deviation of individual values[b]	6.0%
Repeatability r[c]	16.8%

[a] $\frac{\text{difference}}{\text{mean}} \times 100$

[b] $\text{P.S.D.} = \sqrt{\frac{\sum d}{2n}}$ where d = % difference and n = no. of pairs*

[c] $r = 2\sqrt{2} \times \text{standard deviation}$

Note that differences and standard deviations must be shown on a percentage rather than an absolute basis because peroxide values vary with fuel and time. The agreement shown by these data represents the repeatability of the analytical method - as applied to jet fuels. The repeatability "r", as used by ASTM, can be calculated from the standard deviation as shown above. It is defined as "the difference between two successive test results, obtained by the same operator with the same apparatus under constant operating conditions identical test material would, in the long run, in the normal and correct operation of the test method, exceed the following values only in one case in twenty: 0.15X, where X = the average of the two test results." The 16.8 percent above compares closely with 12.2 percent for the control sample in this round robin, 9.8 percent in the second round robin (see below), and 15 percent stated in ASTM Method D-3703-85 for "r".

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* J. H. Youden, Statistical Methods for Chemists, Krieger Publishing Co., Huntington, New York, 1977.

Pratt & Whitney and Southwest Research Institute also carried out some repeat analyses one to four days later than the originals. Since the peroxide values were changing very rapidly with stress time, it is not possible to compare these paired values. However, when graphed as a function of the number of days at 65°C, the Pratt & Whitney data support the conclusion above that the bottle differences do represent real differences in reaction rates between bottles and are not due to sampling or titration techniques. Furthermore the percent spreads for repeat sets of triplicates were as great as for the initial set. On the other hand, the Southwest Research analyses showed appreciable decreases as well as increases with the additional one to three days at 65°C.

b. Variability of Triplicate Fuel Samples (Bottles)

Variations between triplicate bottles as expected were significantly greater than the analytical variability. It is obvious that bottle differences were real. These variations are shown in two ways. In Appendix H, Table H-I, variations greater than 1.5 to 1 and greater than 3 to 1 are indicated by superscripts on the averages. Including cases where all three bottles were zero, and excluding a few cases where peroxide numbers were small and of questionable significance, 62 percent of variations were less than 1.5 to 1, 17 percent were 1.5-3 to 1 and 13 percent were greater than 3 to 1. Table H-II shows the percent difference between the highest and lowest of each set of triplicates. These vary from 0 to 302 percent of mean with an average of 45 percent (40 percent is equivalent to 1.5 to 1). The average spread between duplicate bottles in the previous round robin was 16 percent. This was based on fewer data and is not altogether comparable here. Triplicate variability by either method above is only a little higher (possibly not significantly) for the high peroxide fuels (#4-7) and slightly lower for the low fuels (#1, 2, 3, 8, and 9).

The values in Appendix H, Table H-II varied significantly between laboratories as follows (for all fuels and stress times):

Laboratory	Mean	Std. Dev.
NRL	66%	84%
NAPC	68	93
P&W	16	21
duPont	16	22
Texaco	26	22
NIPER	77	82
SwRI	60	77
Exxon	38	57
Average	45%	57%

Note: "Mean" and "Std. Dev." refer to all the values listed in Table H-II for each laboratory

Also the repeatability "r" (i.e., within sets of triplicates, or within laboratories) was calculated for some representative combinations of fuel and stress time where the peroxide numbers were not zero. Values obtained from the data at four weeks, for example, varied from 20 to 461 percent of mean with an average of 209 percent. Note that "r" is calculated as $2\sqrt{2}$ times the pooled standard deviation of triplicate sets, s_w.

c. Variation Between Laboratories

Variations between laboratories were appreciable and greater than the variability of triplicates. Also they were greater than in the second round robin, which produced much less data. Averages for each fuel, time period and laboratory are plotted in Figures 1-9. Some points or labs in the plots appear to be outliers, e.g., NAPC - fuels 2, 3, 8, 9 and Texaco - fuel 5. A rough measure of the interlab variability is the ratio of the highest to the lowest lab using the averages of triplicates. This ratio exceeded 10 in a number of sets and even exceeded 100 in a few cases. In cooperative program 2 the ratios were mostly in the range 3:1 to 10:1. The current data also show that with longer stress times and consequently higher peroxide levels the ratio did not increase. In other words the relative variation between labs was as great at low peroxide levels as at high levels. The reproducibility "R" for all labs was calculated for particular combinations of fuel and stress time. Using all fuels at four weeks, R was 311-909 percent of mean with an average of 515 percent. "Mean" is the mean of the eight labs for each fuel.

The data reveal that biases between laboratories do exist, ie., some laboratories fairly consistently found higher or lower peroxide than others. For example, duPont and Pratt & Whitney were lowest in almost all cases. Texaco and NAPC were highest with five of the fuels and NIPER with three. However, NAPC was high with the low fuels and low with the high fuels while Texaco and NIPER were high with the high fuels and low with the low fuels. NAPC's high values at six weeks may be related to the fact that analyses at six weeks (and "C" bottles at four weeks) were performed by a different operator. With fuels #6 and #7 there was a sharp division into a high group (Texaco, NIPER, NRL) and a low group (duPont, Pratt & Whitney, NAPC). These results correlate generally with those from the control sample (see below).

Fuels which peroxidized readily were replotted in Figures 10-14 on an expanded scale. With fuels #5-7 the labs found considerable variation in induction time. "Induction time" refers to the time (one to four weeks here) when the production of peroxides changed from a slow rate to a fast rate. This variable induction period explains much of the variation between laboratories.

d. Control Sample

As indicated above, a control sample was prepared and portions were distributed to the laboratories to obtain data on the repeatability of the analytical method used in the accelerated test program. The original data are listed in Appendix H, Table H-III, with averages and percent range added. Corresponding times for stressed samples are noted only for identification purposes. The control samples were directed to be stored in a refrigerator and no change with time was expected and none was found except in the case of NAPC. Here use of three different operators may have been a factor.

The percent range or spread of each set of quadruplicates varied from 2.0 percent to 17.0 percent with an average of 7.3 percent. Compare with the average of 6.2 percent in Round Robin 2. The pooled standard deviation of individual values (s_w) was 0.0905 or 4.3 percent of the mean peroxide number of 2.09 meq/kg. This agrees well with the 6.0 percent shown above for duplicate fuel analyses. The comparable value of s_w in the second round robin was 3.5 percent. Repeatability "r" for the current data then equals $2\ 2s_w$ = 12.2 percent. The foregoing refers to "immediate repeatability". These values may be compared with the values for duplicate fuel analyses above, which also indicate the immediate repeatability of the analytical method. Calculated values for non-immediate repeatability (i.e., the variation between averages at different times, as two and four weeks, at the same laboratory) were 2.2 percent average range and 1.7 percent for the pooled standard deviation.*

Reproducibility (the variation between laboratories) is shown by the following data (extracted from Table H-III of Appendix H):

Laboratory	Average Peroxide No.
NAPC (2, 6 weeks)	3.33 meq/kg
SwRI	2.41
NIPER	2.35
NRL (25 ml)	2.31
Texaco	2.14
P&W	2.04
DuPont	1.87
Exxon	1.54
Grand average (excluding NAPC)	2.09

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* $$\frac{\sqrt{\frac{\sum d^2}{2n}}}{\text{grand average}} \times 100$$

Statistical values calculated from the data in Table H-III, Appendix H, and corresponding values for Cooperative Program 2 are shown below:

Statistic	Round Robin 3	Round Robin 2
Grand average, meq/kg	2.09	9.91
Spread between averages	0.87 = 42%*	1.31 = 13%*
s_b**	40.6%	14.6%
Reproducibility R (2 2 s_b)	115%	41%
Average spread within labs	7.3%	6.2%
s_w	4.3%	3.5%
Repeatability r (2 2 s_w)	12.2%	9.8%

* Percent of average peroxide number for all labs (2.09 and 9.91).

** Standard deviation between labs. Calculated as shown in Statistical Methods for Chemists, p. 32, J.H. Youden, Krieger Publishing Co., Huntington, N.Y., 1977

Note: NAPC data in Round Robin 3 were excluded.

Obviously the variation between laboratories is much greater than that within laboratories. See also the comments above under interlab variation of fuel results concerning laboratories that gave more or less consistently high or low results. The reproducibility R = 115 percent above is disappointingly high and is to be compared with the 41 percent found in the second round robin and the 60 percent stated officially for ASTM Method D-3703. The calculation of R from s_b depends on the definition of R, namely, "The difference between two single and independent results, obtained by different operators working in different laboratories on identical test material would, in the long run, in the normal and correct operation of the test method, exceed the following values only in one case in twenty: R = 0.60X, where X = the average of two test results."

e. Effect of Sample Size

Some observations on the control sample (Table H-III, Appendix H) indicated that peroxide number varies (inversely) with sample size:

Laboratory	Sample Size	Average Peroxide No.
NRL	10 ml (8.06 g)	2.583
	25 ml (20.16 g)	2.310
	50 ml (40.3 g)	2.060
NIPER	15 g	2.473
	21 g	2.370
	23 g	2.324
	26 g	2.311
	28 g	2.310
	31 g	2.264

The NRL and NIPER data give a single smooth plot for P.N. vs. sample size. Other laboratories did not report sample size. Unrelated experience at NRL with peroxide determination in fuels has shown no such effect. This effect may explain some of the differences between laboratories.

f. Evaluation of Go/No-Go Test Potential

The military specification for Aviation Turbine Fuel* sets a peroxide number maximum of 1.0 meq/kg for JP-5. We therefore examined the Round Robin 3 data to evaluate the P.N. requirement of 1.0 vs. the various test times at 65°C.

Table II lists the number of laboratories which exceeded the 1.0 limit at the different test times. A high number, 7 or 8, indicates agreement between laboratories with respect to failure (P.N. > 1.0). Note that Fuels #4 and #6 were rated as failing in three weeks by all labs (7 of 7) and Fuels #5 and #7 failed on most tests at four weeks. However, two fuels (#1 and #9) which showed good stability at three weeks or less, were rated as fails by one lab each at four weeks. At longer times (six weeks), additional failures were observed.

On the basis of the bulk of the data, Fuels 1, 2, 3, 8, and 9 can be classified as satisfactory and Fuels 4, 5, 6 and 7 rated as unacceptable. At stress times of three or four weeks, a peroxide number of 1.0 meq/kg is a good criterion for distinguishing the two sets of fuels. Although other values of the P.N. could be considered to improve the distinction between good and bad fuels, a P.N. of 1.0 is favored on the basis of elastomer tests.

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* MIL-T-5624L with Amendment 2, "Turbine Fuel, Aviation, Grades JP-4 and JP-5," August 10, 1983.

Summarizing for the two sets of fuels:

(a) At three weeks, poor fuels exceeded a P.N. of 1.0 in 26 of 28 fuel/lab combinations

(b) At three weeks, good fuels exceeded a P.N. of 1.0 in 0 of 28 fuel/lab combinations

(c) At four weeks, poor fuels exceeded a P.N. of 1.0 in 32 of 32 fuel/lab combinations

(d) At four weeks, good fuels exceeded a P.N. of 1.0 in 2 of 32 fuel/lab combinations.

Data from Round Robin 2 supports the Go/No-Go findings from the current exercise. In the earlier cooperative tests, one fuel was markedly unstable at 65°C and four were classified as stable. All six labs participating in that exercise found more than 1.0 meq/kg of hydroperoxide for the one bad fuel at three weeks (also at two weeks) and none of the labs found more than 1.0 meq/kg for the other four fuels at three weeks. One laboratory failed one of the acceptable fuels at both five and eight weeks.

IV. CONCLUSIONS

Based on the cooperative work reported herein, the 65°C accelerated test readily distinguishes between stable and unstable fuels in approximately three weeks stress time. Consequently it appears useful for screening jet fuels for their long-time oxidation stability. Thus this test is recommended as a Go/No-Go test. On the other hand the variability of results within and between laboratories would seem to preclude its use as a precise quantitative tool.

In more detail, the nine fuels examined in this cooperative program can be divided into five acceptable and four unacceptable fuels on the basis of the overall pattern of fuel behavior. Using a criterion of a Peroxide Number of 1.0 meq/kg, six laboratories out of seven successfully distinguished between the two groups of fuels at three weeks and eight out of eight at four weeks.

Data were obtained on the repeatability r (within laboratories) and reproducibility R (between laboratories) of the analytical method, ASTM D3703, applied to jet fuels by measurements on a non-heat-stressed control sample. The value for r was 12 percent of mean. This was confirmed by the corresponding value of 17 percent for 76 pairs of duplicate fuel analyses. On the other hand the repeatability in the accelerated test between triplicate stressed fuel samples within laboratories was 20-461 percent of mean in selected cases of fuel and stress time. The reproducibility R between laboratories was 272-909 percent of mean. Some of the latter variability was due to laboratory bias, i.e., some laboratories were consistently high or low. Thus the analytical variability was small while variability between identical stressed fuel samples and between laboratories was great.

T A B L E S

AND

F I G U R E S

TABLE I

TEST FUELS

Fuel No.	Type	Source	Hydrotreatment
1	Jet A	Texaco	Mildly Hydrotreated
2	Blending Stock	Shell, Thornton, UK	Moderately Hydroprocessed
3	Blending Stock	Shell, Thornton, UK	Severely Hydroprocessed
4		Petro-Canada, Montreal	Hydrotreated
5	Shale	Wright-Patterson AFB	Hydrotreated
6	Jet A Blending Stock	ESSO Petroleum Corp. Research Division, Sarnia, Ontario	Hydrofined
7	Jet A Blending Stock	ESSO Petroleum Corp. Research Division, Sarnia, Ontario	Hydrocracked
8	JP-5	Exxon, Baton Rouge	No Hydrotreatment
9	JP-5	Exxon, Benicia	Moderately Hydrotreated

TABLE II

ACCELERATED TEST TIME NEEDED TO DISTINGUISH BETWEEN STABLE AND UNSTABLE JET FUELS

Fuel No.	No. of Labs With Peroxide Number Greater Than 1 meq/kg — Weeks Stressed at 65°C				
	1	2	3*	4	6
1	0	0	0	1	2
2	0	0	0	0	3
3	0	0	0	0	0
4	2	8	7	8	8
5	0	2	6	8	8
6	2	7	7	8	8
7	0	4	6	8	8
8	0	0	0	0	0
9	0	0	0	1	3

*7 labs reported instead of 8.

Note: Fuels #1,2,3,8,9 are classified as stable fuels and #4-7 as unstable fuels.

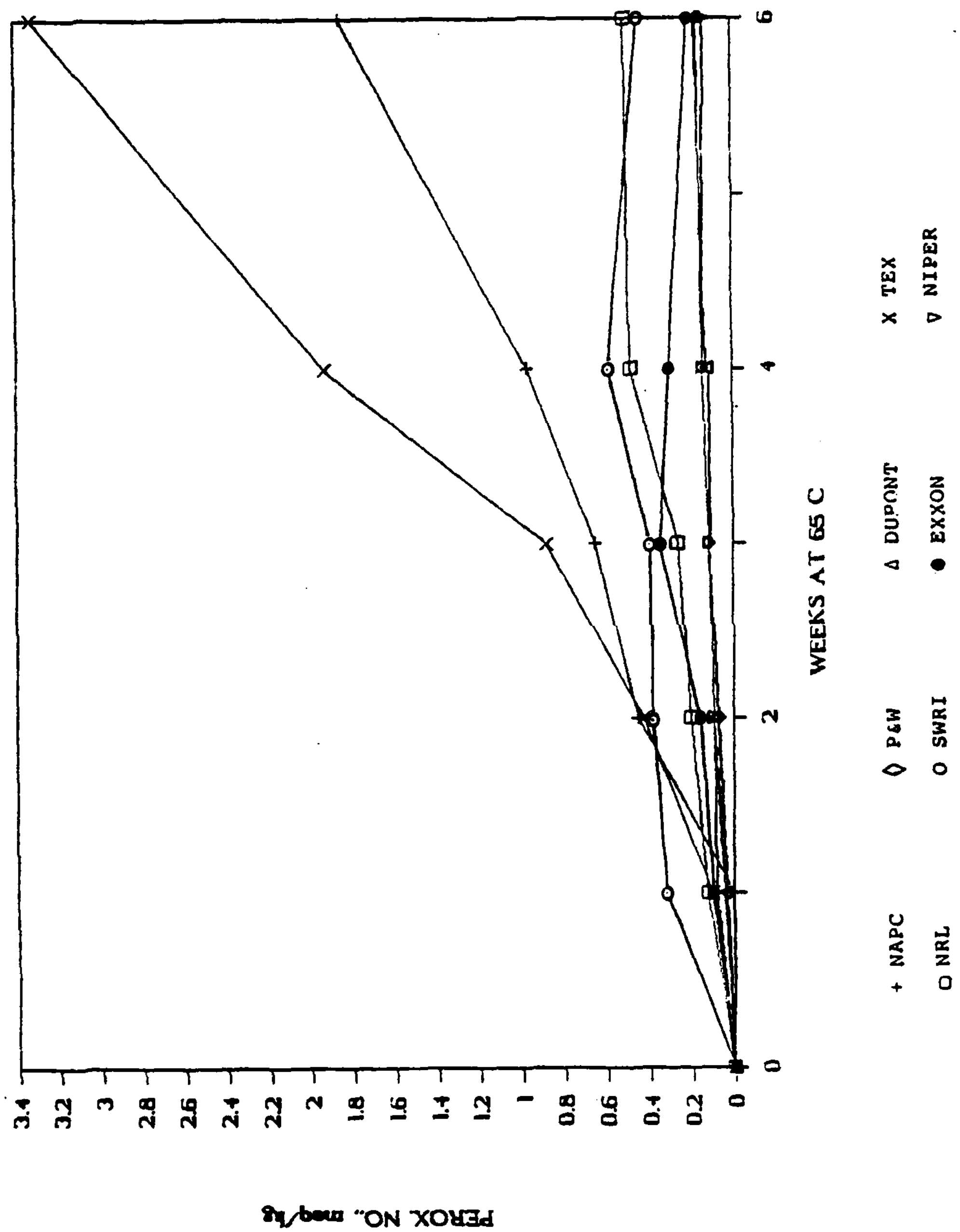


Fig. 1 — Average Peroxide Number vs Stress Time—Fuel 1

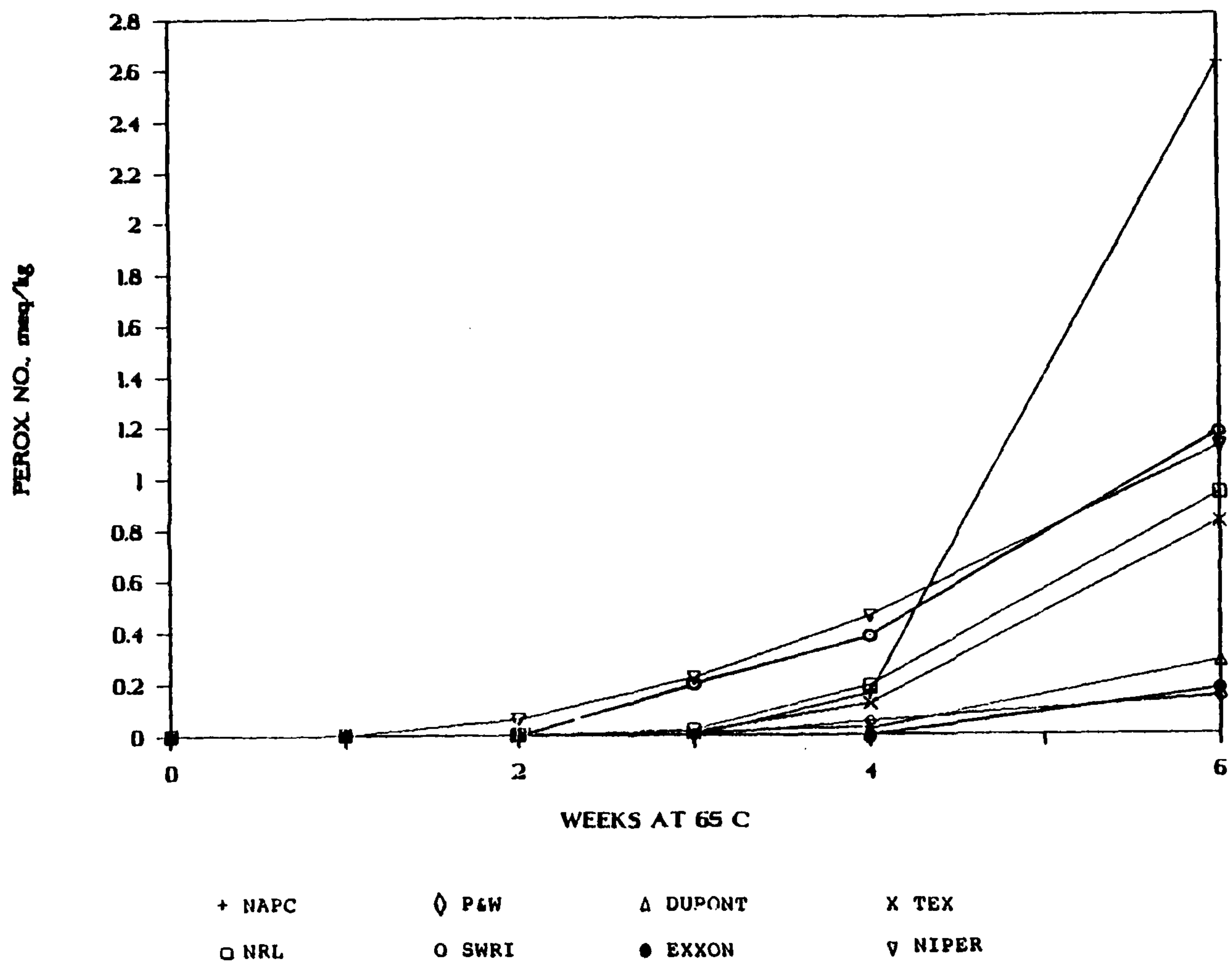


Fig. 2 — Average Peroxide Number vs Stress Time—Fuel 2

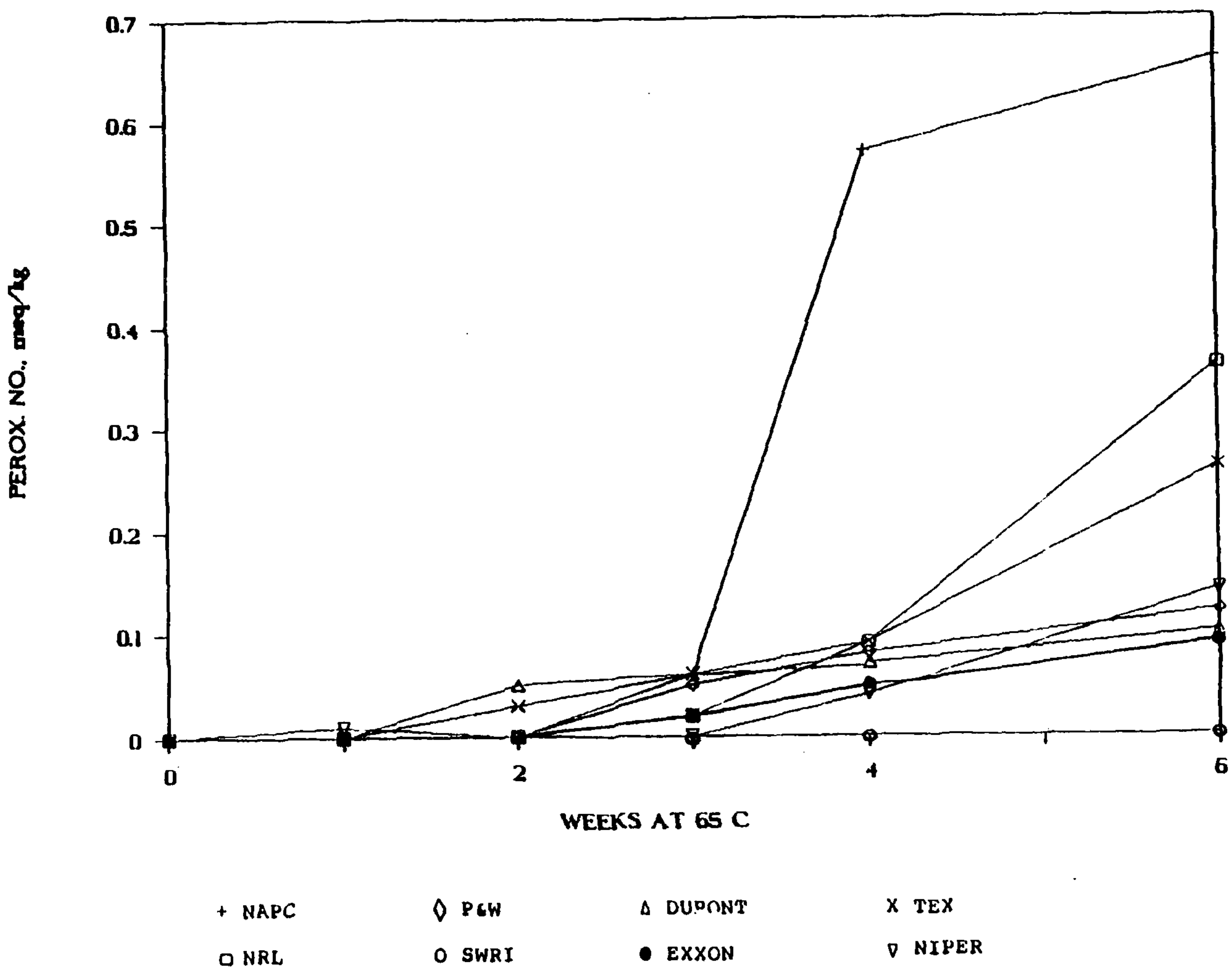


Fig. 3 — Average Peroxide Number vs Stress Time—Fuel 3

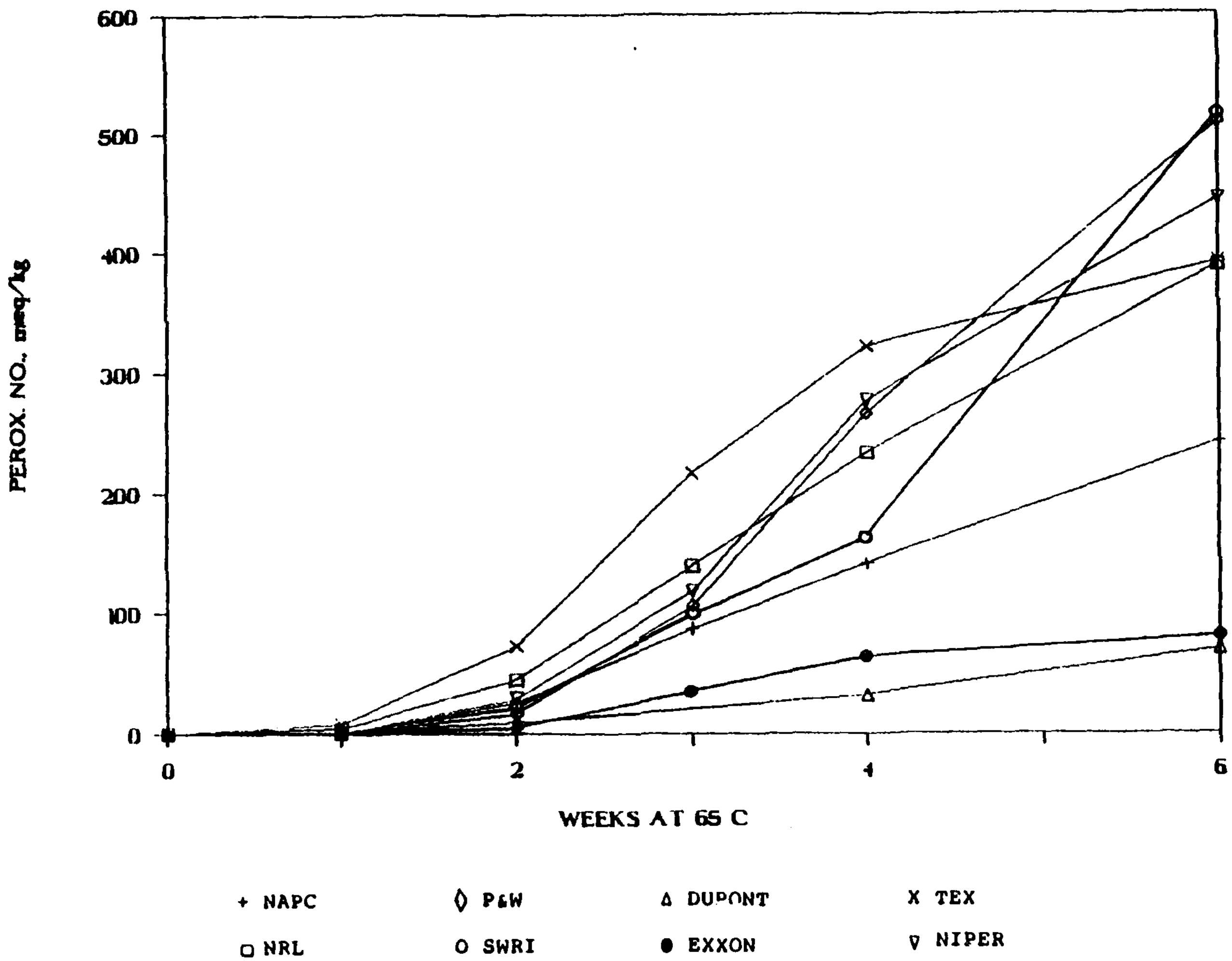


Fig. 4 — Average Peroxide Number vs Stress Time—Fuel 4

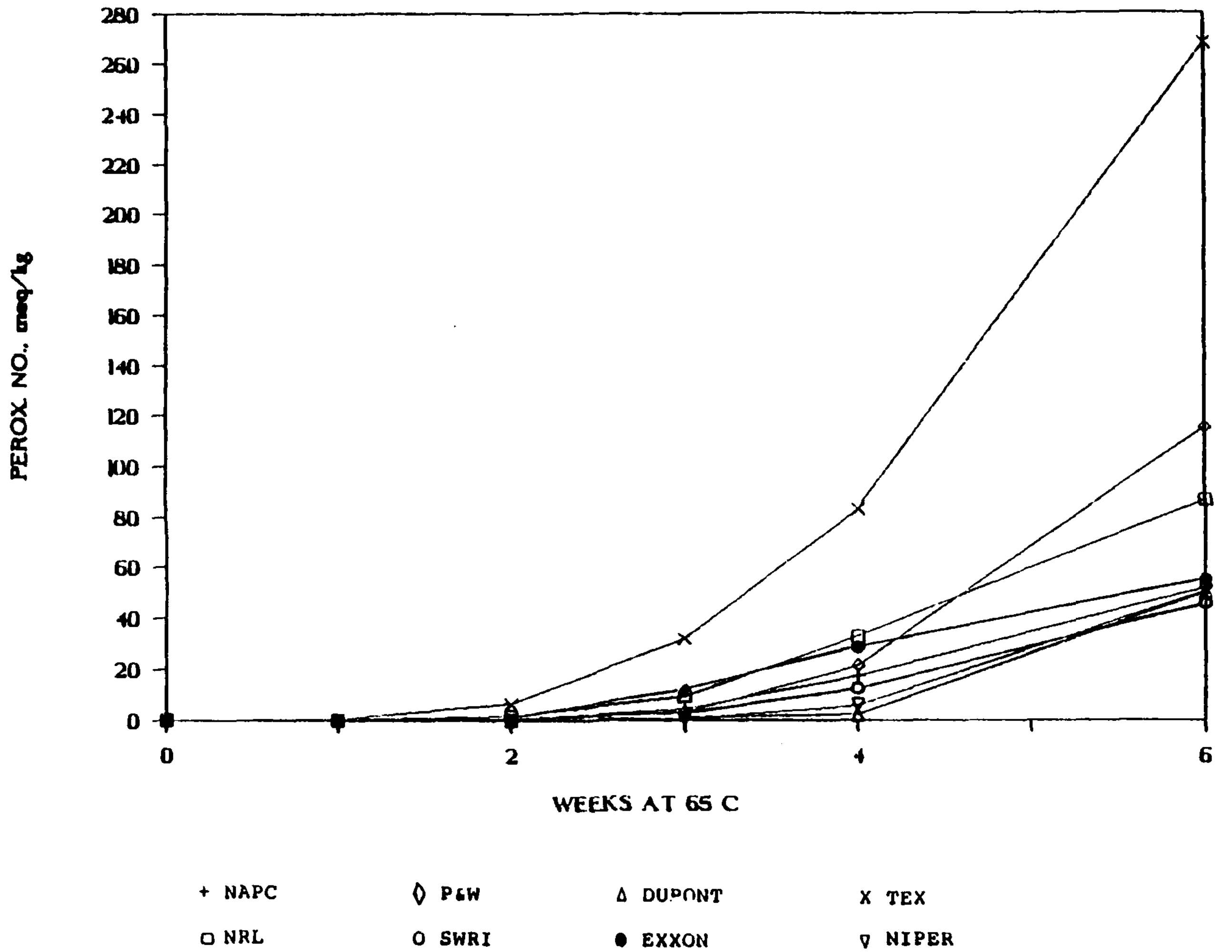


Fig. 5 — Average Peroxide Number vs Stress Time—Fuel 5

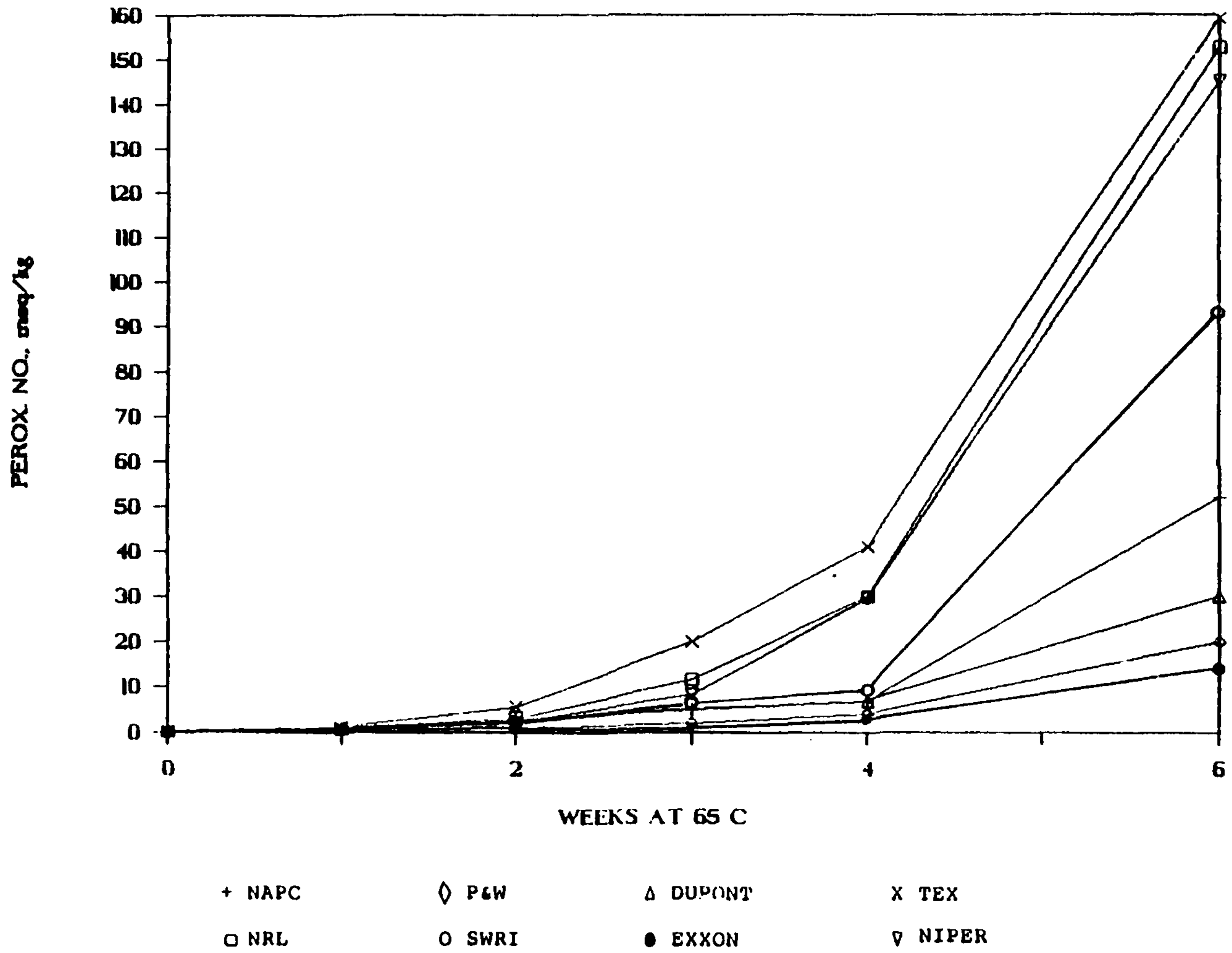


Fig. 6 — Average Peroxide Number vs Stress Time—Fuel 6

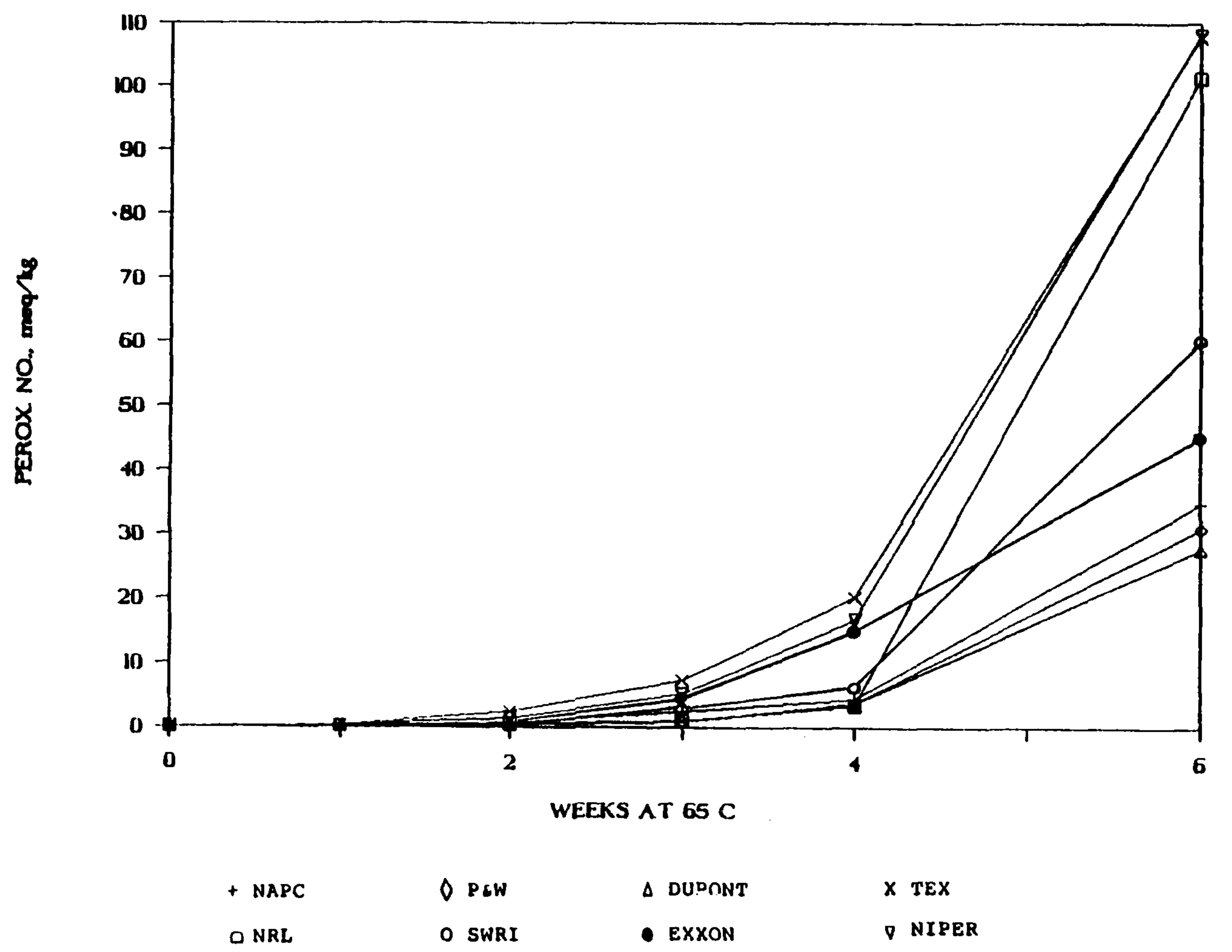


Fig. 7 — Average Peroxide Number vs Stress Time—Fuel 7

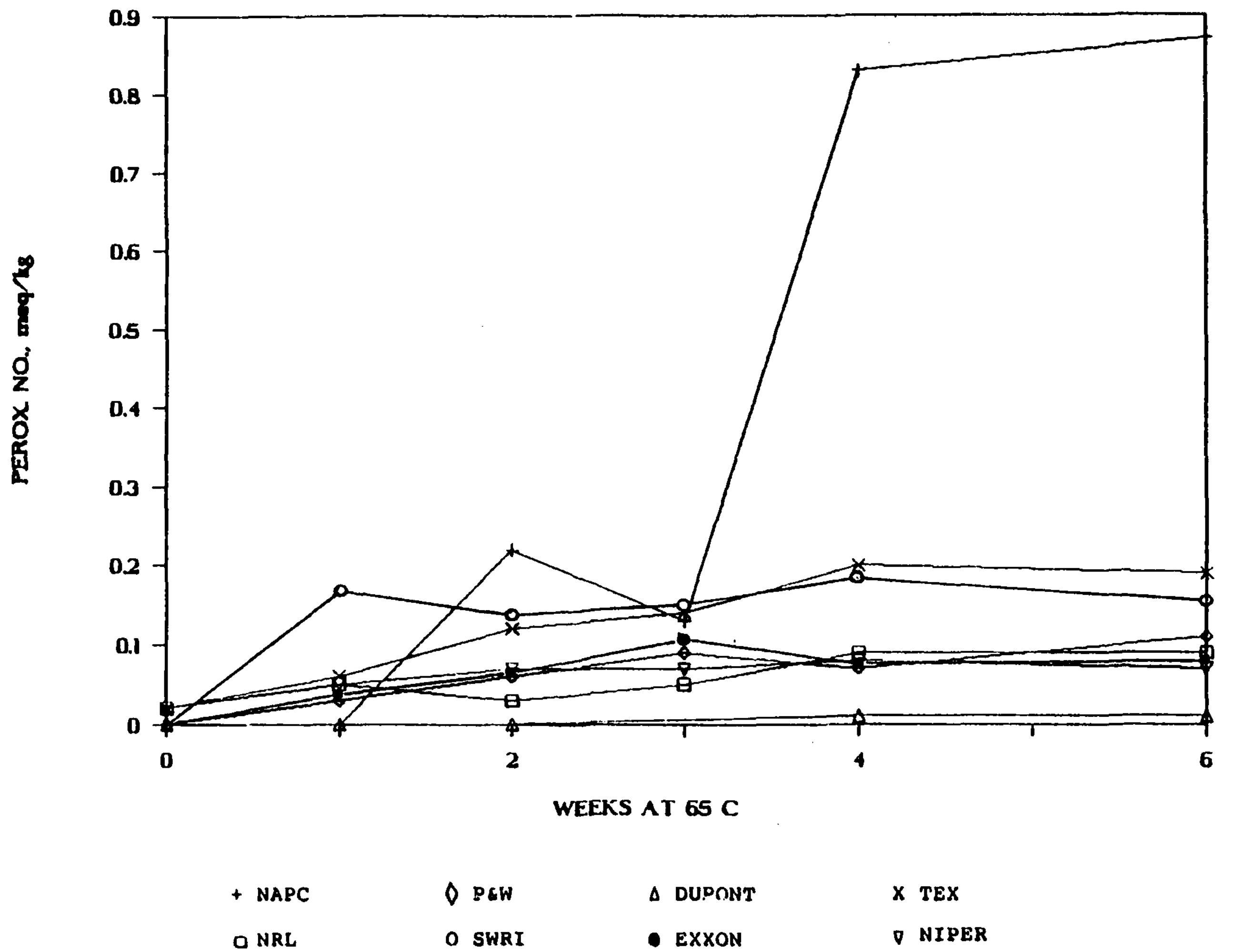


Fig. 8 — Average Peroxide Number vs Stress Time—Fuel 8

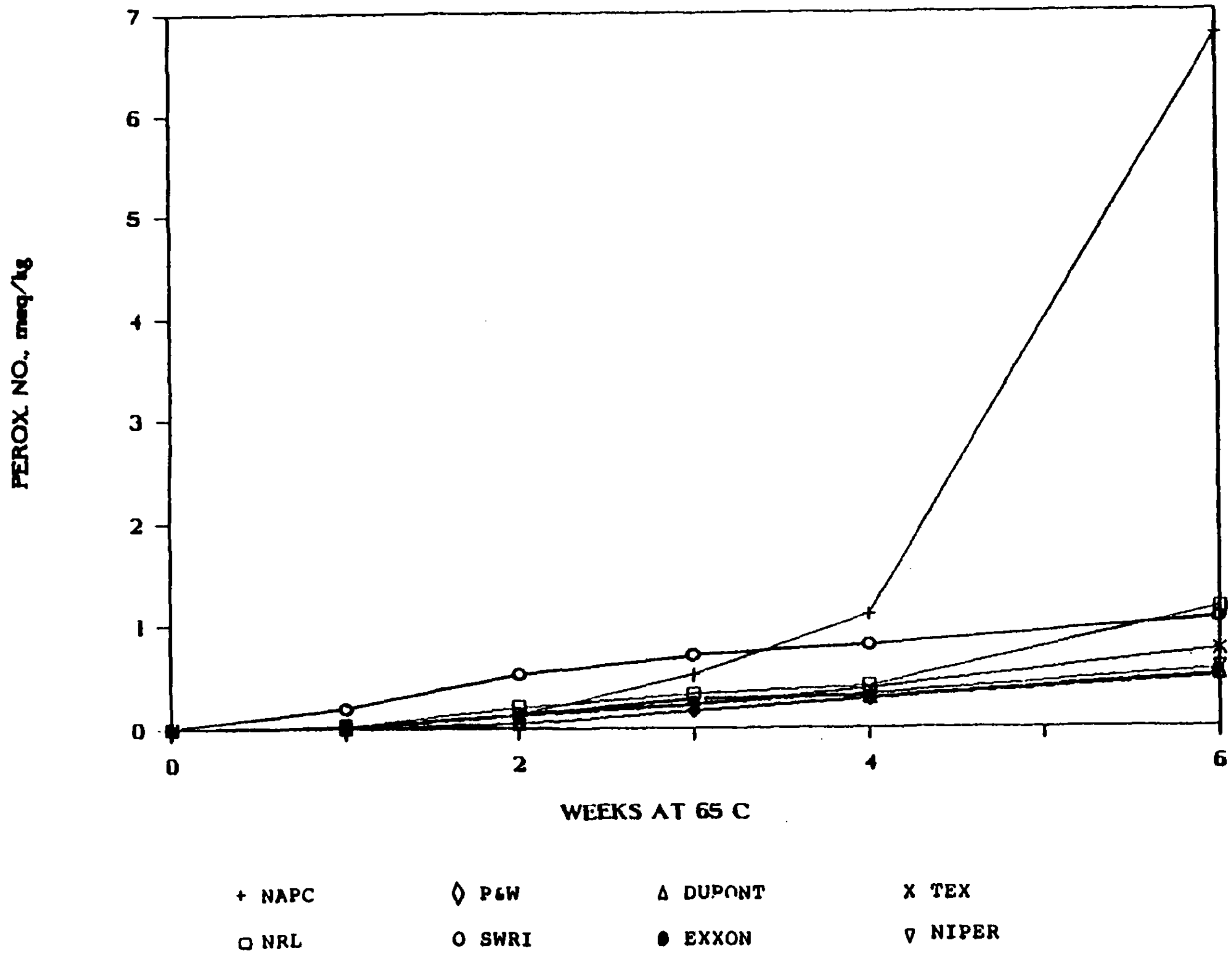


Fig. 9 — Average Peroxide Number vs Stress Time—Fuel 9

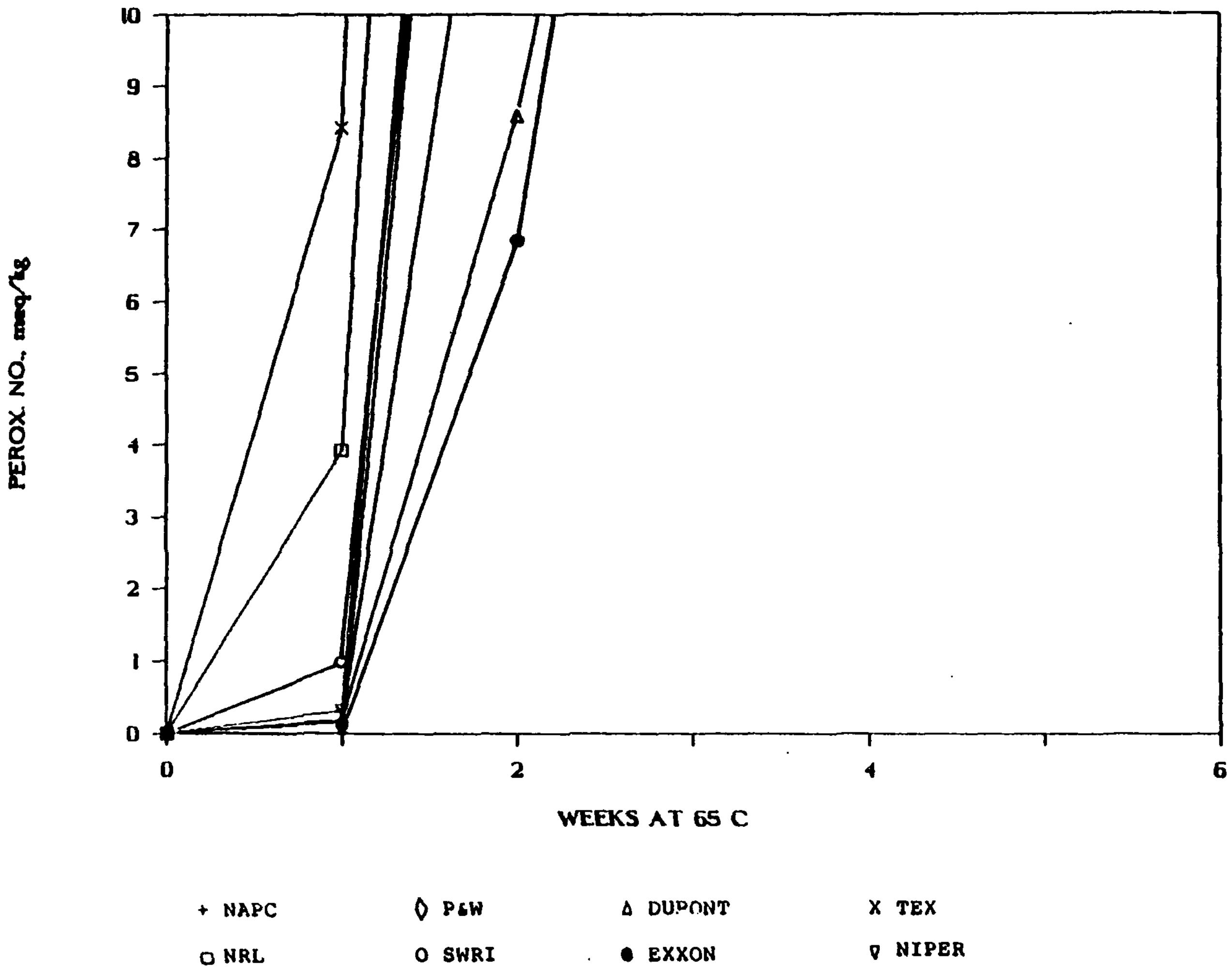


Fig. 10 — Average Peroxide Number vs Stress Time—Fuel 4—Expanded Scale

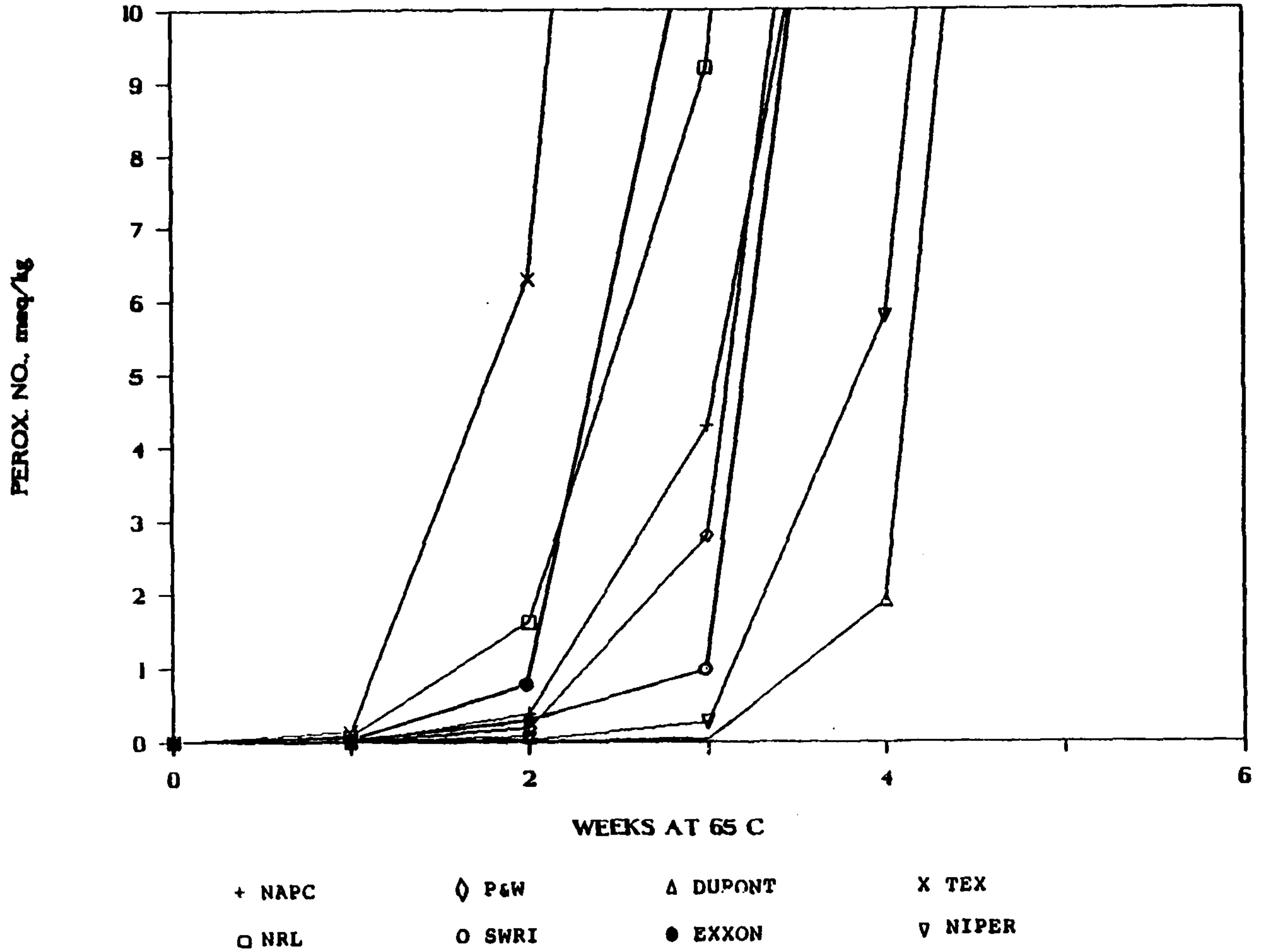


Fig. 11 — Average Peroxide Number vs Stress Time—Fuel 5—Expanded Scale

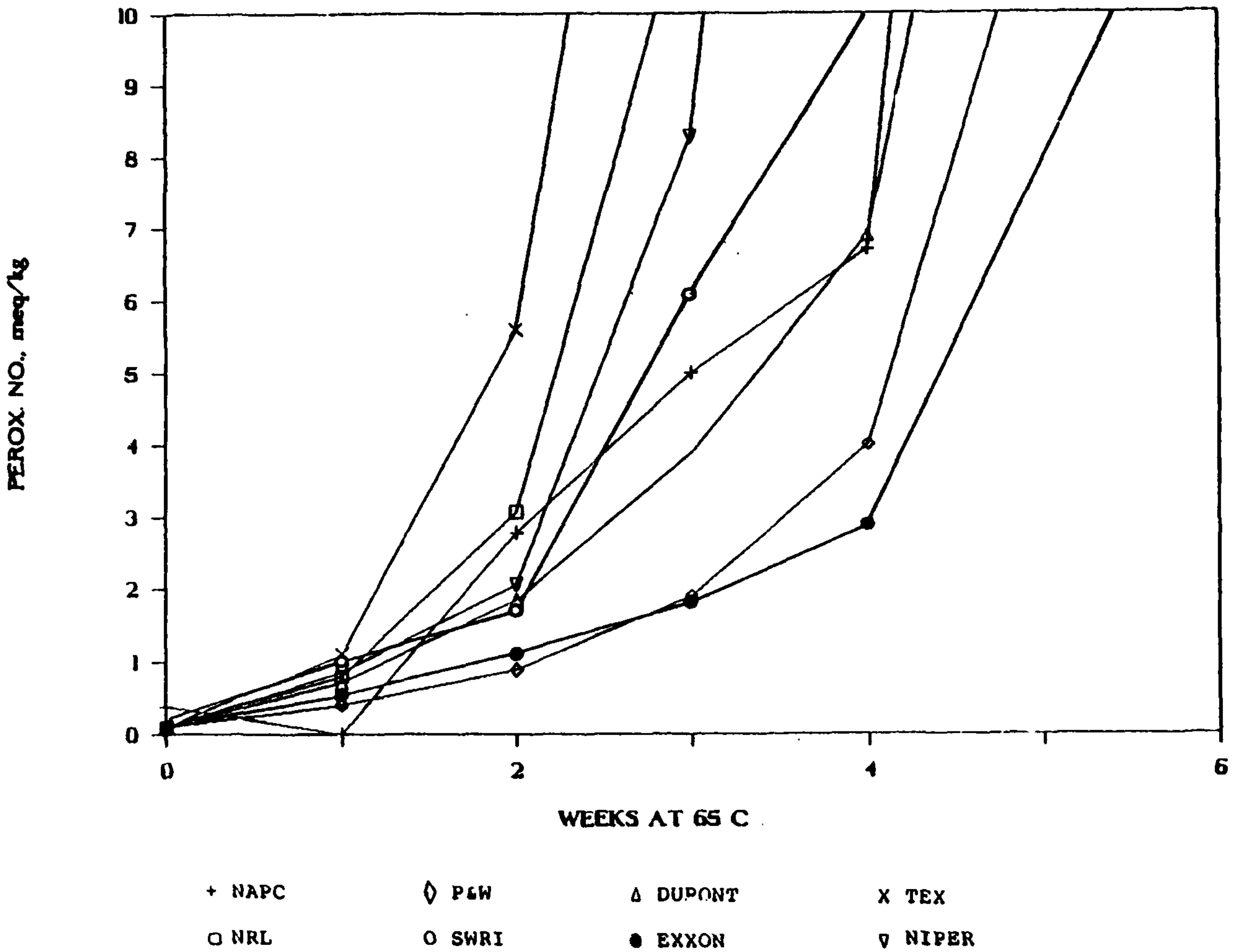


Fig. 12 — Average Peroxide Number vs Stress Time—Fuel 6—Expanded Scale

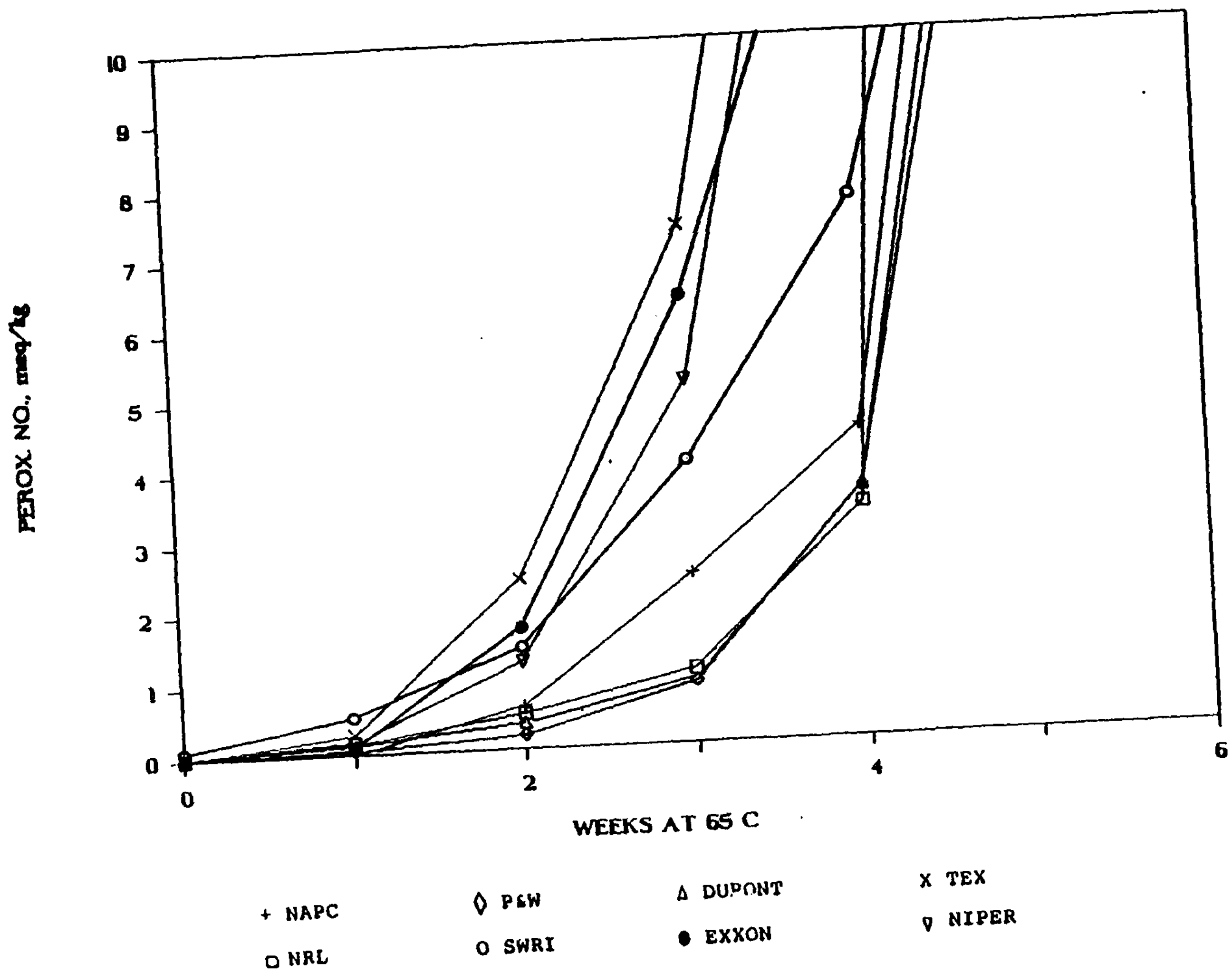


Fig. 13 — Average Peroxide Number vs Stress Time—Fuel 7—Expanded Scale

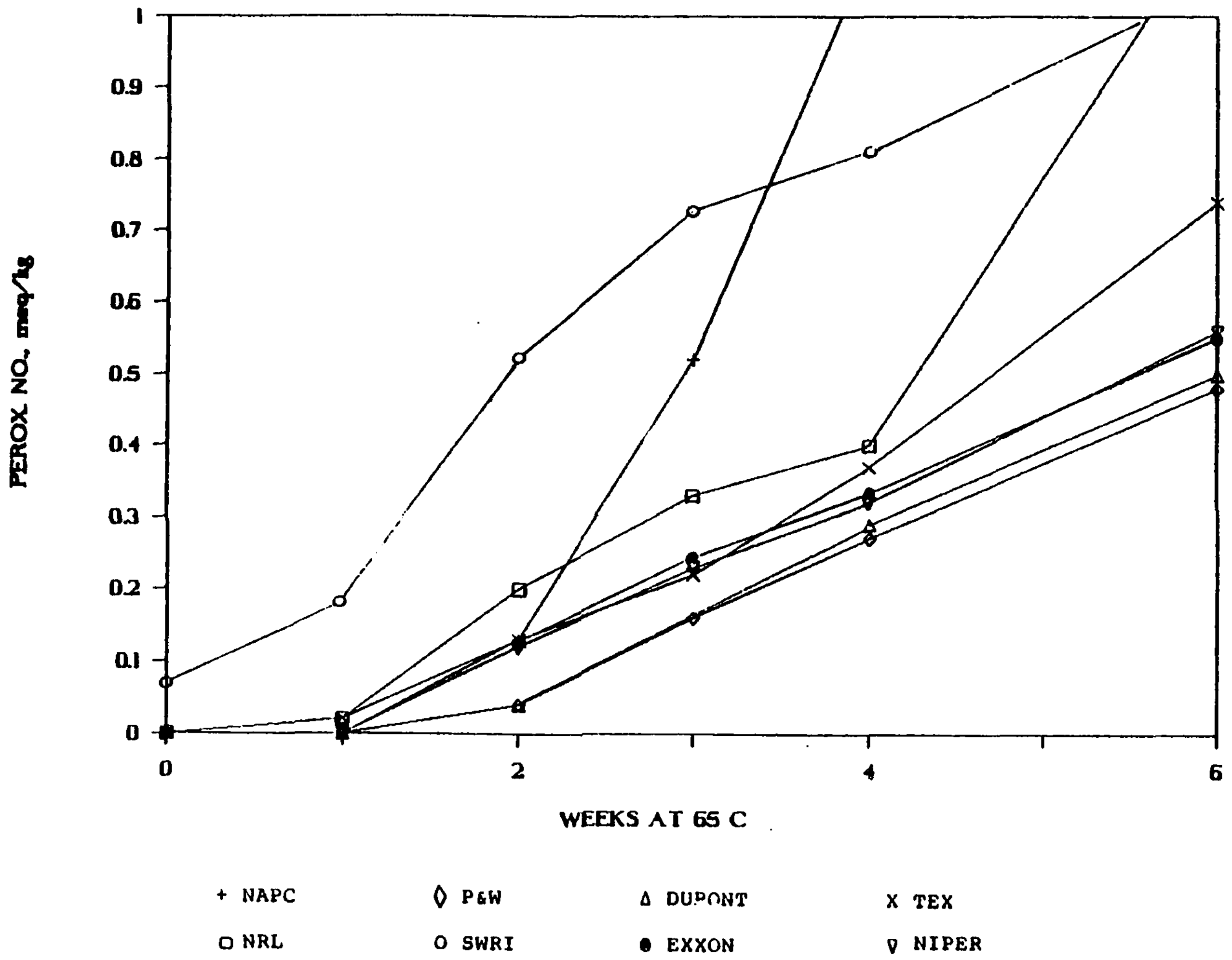


Fig. 14 — Average Peroxide Number vs Stress Time—Fuel 9—Expanded Scale

APPENDIX A

PANEL MEMBERSHIP
AND
PARTICIPATING LABORATORIES

MEMBERSHIP OF THE HYDROPEROXIDE POTENTIAL OF JET FUELS PANEL OF THE CRC OXIDATION STABILITY OF GAS TURBINE FUELS GROUP

Name	Affiliation
J. M. HALL	Geo-Centers, Inc.
W. G. DUKEK	Consultant (Retired from Exxon)
C. P. HENRY	E. I. du Pont de Nemours & Co.
R. E. HILEMAN	Texaco, Inc.
R. W. MORRIS	Air Force AeroPropulsion Labs
K. H. STRAUSS	Consultant
W. A. SUTTON	Ashland Oil Company
L. C. TURNER	Naval Air Propulsion Center
P. A. WARNER	Pratt & Whitney Aircraft

PARTICIPATING LABORATORIES

Cooperative Program 1

Naval Air Propulsion Laboratory	Clarence Nowack
Naval Research Laboratory	Robert Hazlett
Southwest Research Institute	John Goetzinger
Texaco Inc.	Mike Caggiano
Wright-Patterson Air Force Base	Tim Dues, Robert Morris

Cooperative Program 2

E. I. duPont de Nemours	Tayman Phillips
Naval Research Laboratory	Jim Hall
Naval Air Propulsion Center	Linda Craig
Pratt & Whitney Aircraft	Linda Neubauer, Paul Warner
Texaco Inc.	Salvatore Rand
Southwest Research Institute	Pat Cuellar

Cooperative Program 3

E. I. duPont de Nemours & Co.	Tayman Phillips
Exxon Research & Engineering Co.	William Taylor
Naval Research Laboratory	Jim Hall
Naval Air Propulsion Center	Lynda Turner
National Institute for Petroleum and Energy Research	John Goetzinger
Pratt & Whitney Aircraft	Linda Neubauer Paul Warner
Southwest Research Institute	Pat Cuellar
Texaco Inc.	Salvatore Rand

APPENDIX B

REPORT ON STUDIES TO DEVELOP A TEST TO DETERMINE POTENTIAL OF FUEL FOR HYDROPEROXIDE FORMATION

COORDINATING RESEARCH COUNCIL
GROUP ON OXIDATION STABILITY OF GAS TURBINE FUELS
May 1, 1981

R. N. Hazlett and J. M. Hall
Naval Research Laboratory
Washington, D. C. 20375

Studies to Develop a Test to Determine the Potential of a Fuel for Hydroperoxide Formation

The test described is based on experience at Rolls-Royce in the 1960's and made available to the Group by Mr. Arthur Peat.

A jet fuel sample of 250 ml was placed in a clean, brown borosilicate bottle (500 ml). The capped bottle was placed in an explosion-proof oven controlled at 100°C. The bottle was removed periodically from the oven, cooled, and sampled for analysis. Hydroperoxide content was determined by ASTM Method D1563.

Repeatability - Several samples have been stressed in duplicate or triplicate. Both new and used bottles have been utilized but no bias has been observed. Triplicate tests for a Shale-II JP-5 are presented in Figure 1. The three tests are quite comparable particularly during the buildup period (0-5 days). It is noteworthy that this sample, even though it contained a hindered phenol antioxidant, attained high concentrations of hydroperoxide. Further, the peroxide number dropped sharply after reaching maxima in 5 to 10 days.

Three tests with a Jet A (Exxon) are depicted in Figure 2. Again the tests gave very good repeatability. Note the scale difference for this figure. The peroxide numbers rose rapidly in the first two days but peaked at values well below one. This fuel had been hydrotreated but contained no antioxidant.

JP-5 Tests - Nine current production JP-5's were stressed at 100°C. The results for three of the fuels are graphed in Figure 3. All other samples fell within the range shown. Four fuels gave patterns very similar to the upper curve and four others mimicked the lower curve. The maximum peroxide numbers for these fuels, all of which contained antioxidant, were well under one.

Shale-II JP-5 Comparisons - Several samples obtained during the Shale-II refining operation at Sohio were peroxidized. Whereas the repeatability for any one sample was good, similar samples taken at different times exhibited markedly different behavior. Figure 4 illustrates this for four samples, two containing antioxidant and two free of antioxidant. The four samples peroxidized in unique patterns. The antioxidant appears to moderate hydroperoxide formation but the P.N. reached a maximum of 10 for one sample with A.O. A fifth JP-5 sample from the Shale-II refining gave P.N.'s as high as 40 (Figure 1).

Shale-II Diesel Fuel Marine (DFM) Comparisons - The Sohio shale DFM was also subjected to stress at 100°C. The repeatability for one sample is shown in Figure 5. P.N.'s for three different Shale-II DFM's are plotted in Figure 6. The repeatability is good but different samples exhibit great variability. Antioxidant is not a sure control of peroxidation.

Conclusions - The test described gives reasonable repeatability. Further, the test readily distinguishes between different samples. Petroleum derived JP-5's containing antioxidant peroxidize only slightly. Shale-II fuels (JP-5 and DFM) peroxidize readily and antioxidants are ineffective in controlling the behavior of these fuels.

Attachments
Figures 1 through 6

Fig. 1. PEROXIDATION OF A SHALE II JP-5 SAMPLE IN TRIPLICATE

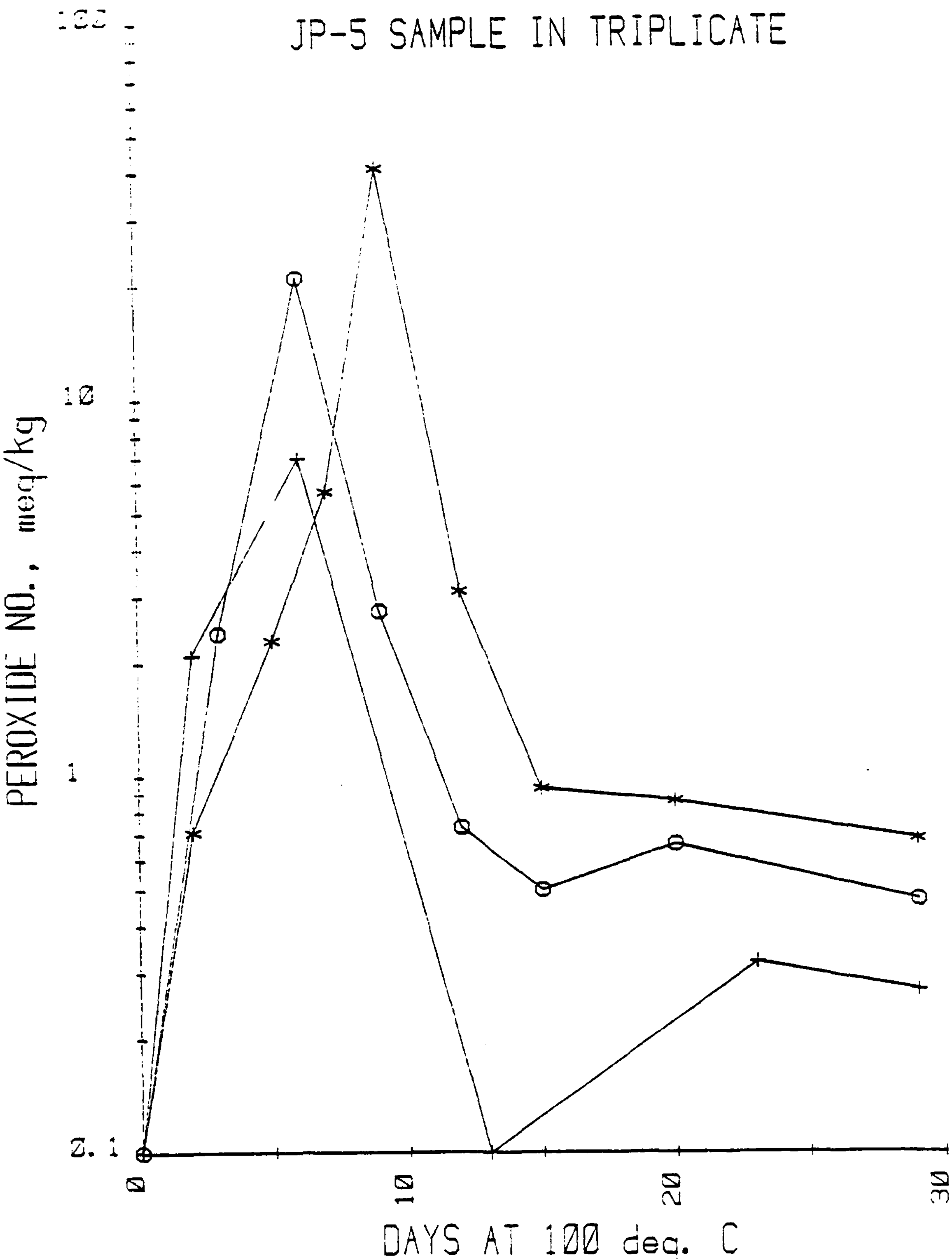


Fig. 2. PEROXIDATION OF EXXON HYDROTREATED JET A w/o ANTIOXIDANT

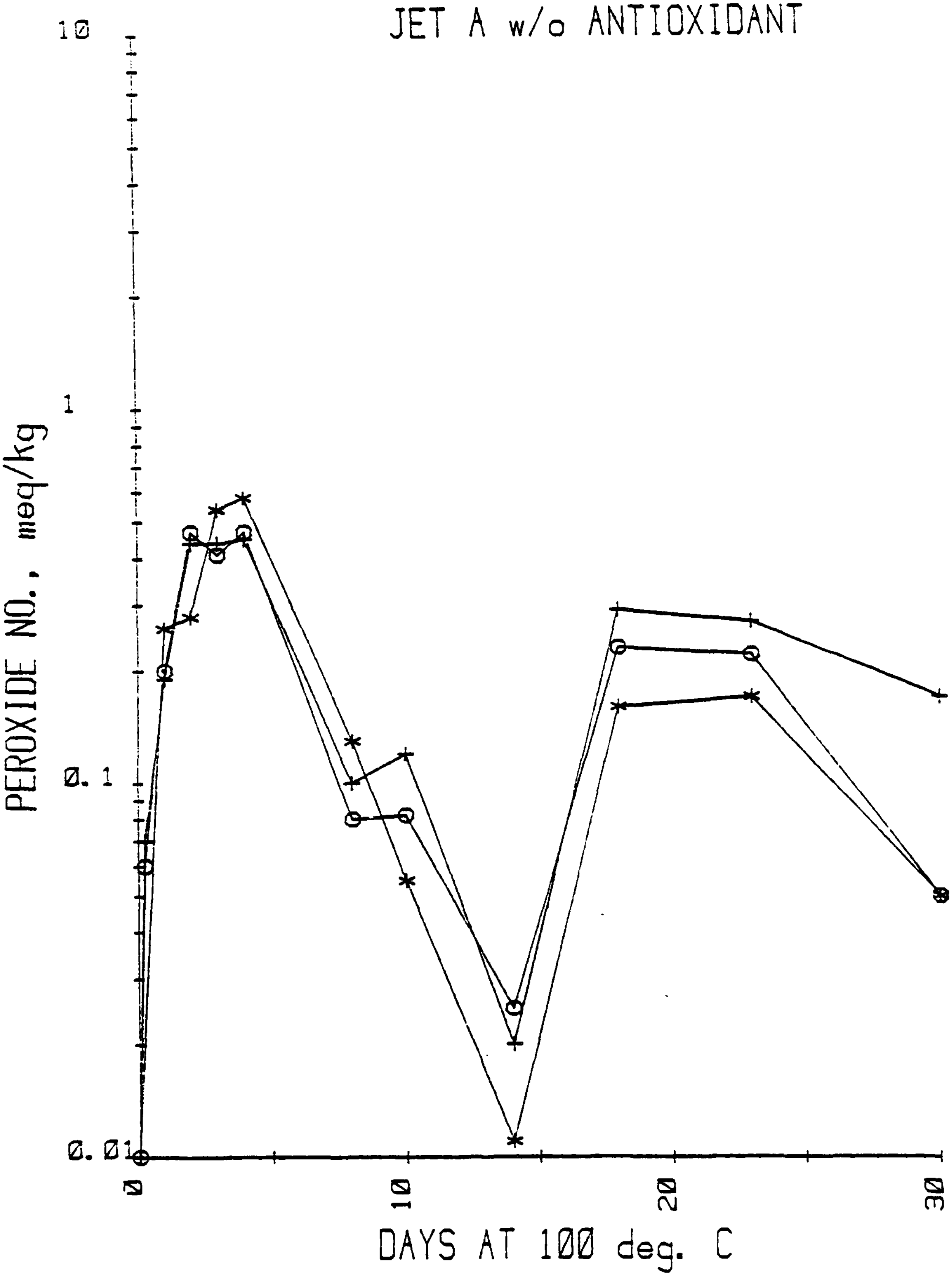


Fig. 3. PEROXIDATION OF 3 PETROLEUM JP-5's

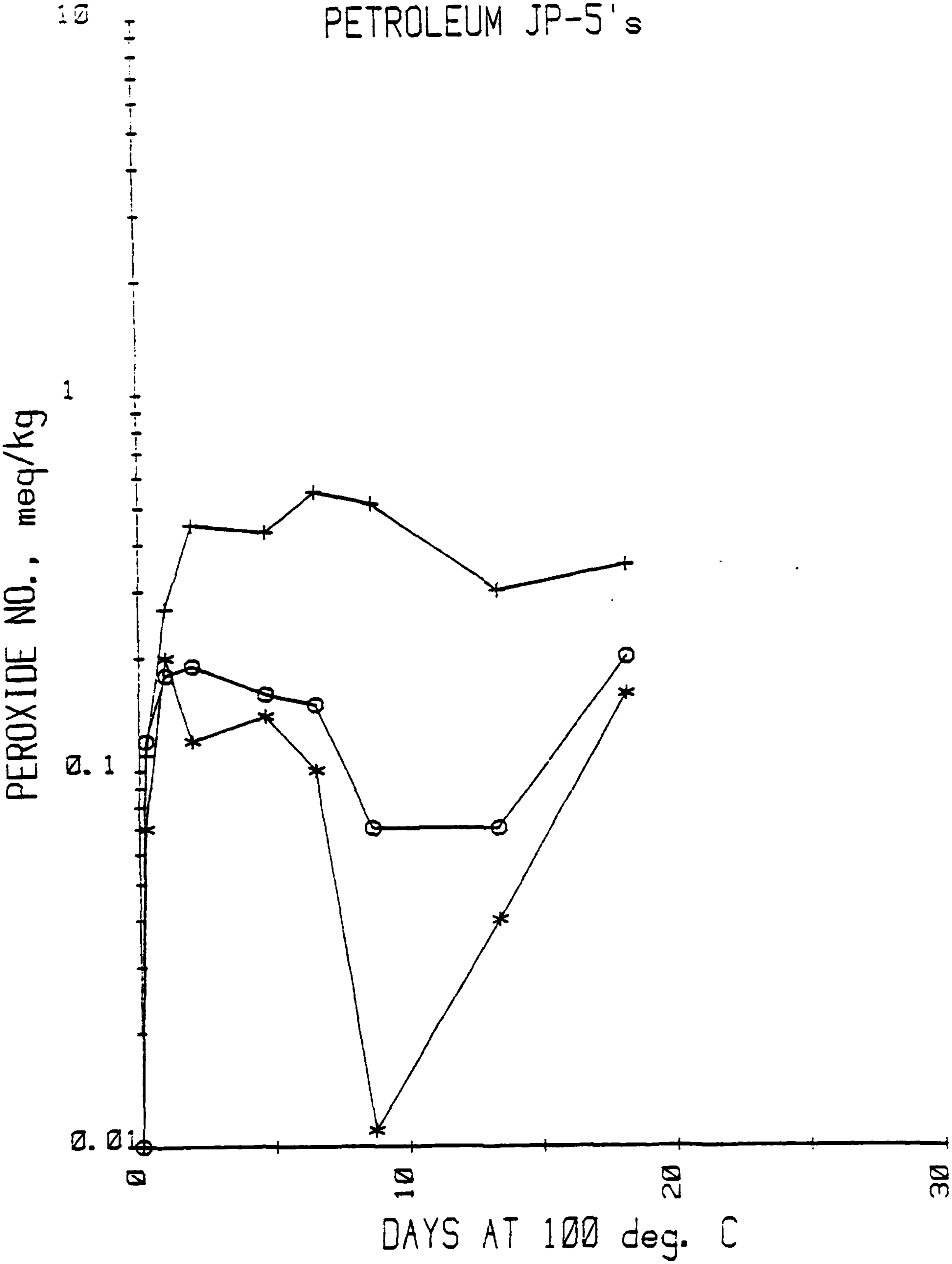


Fig. 4. PEROXIDATION OF 4 JP-5's FROM SHALE II

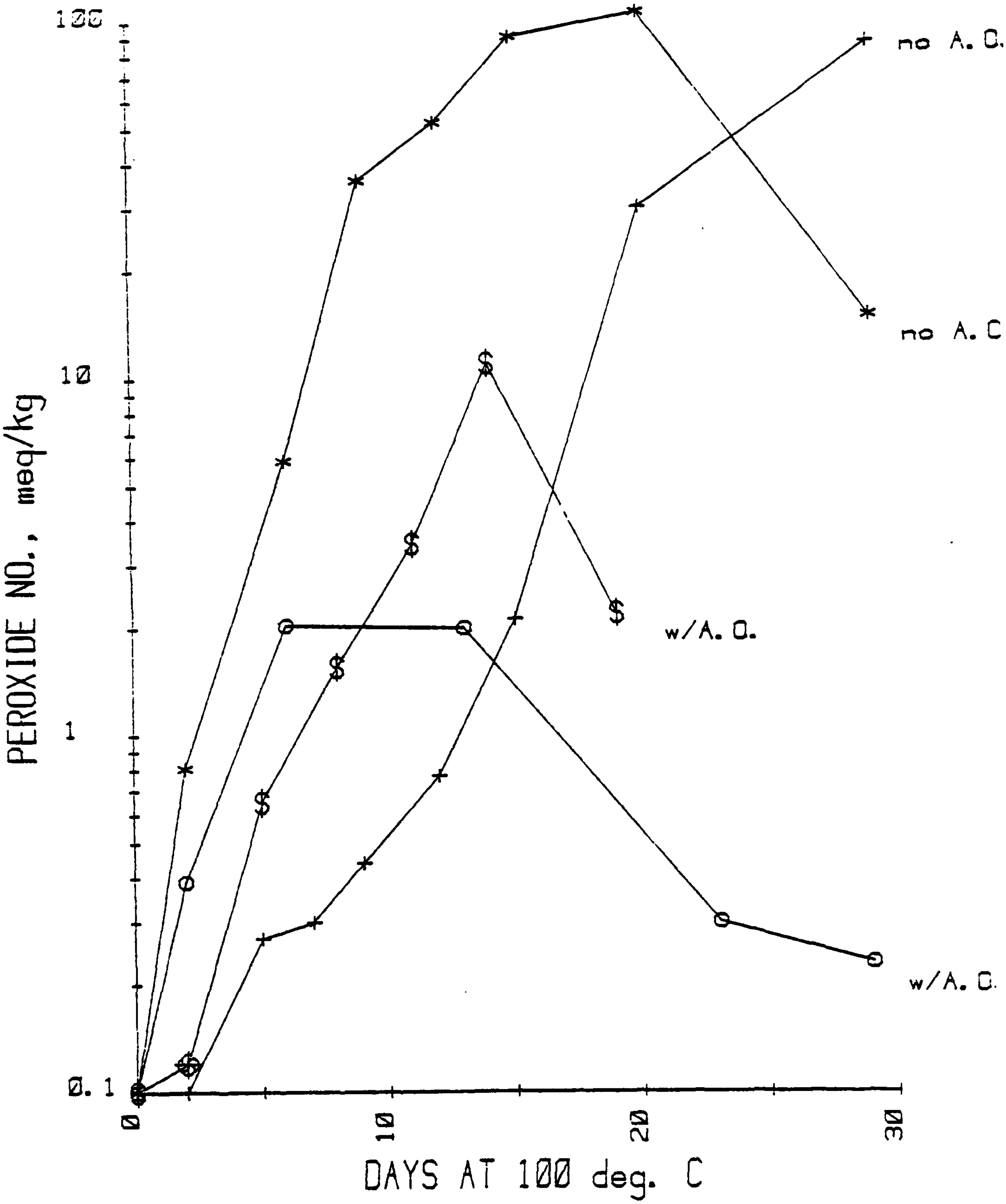


Fig. 5. PEROXIDATION OF A SHALE II DFM SAMPLE IN TRIPLICATE

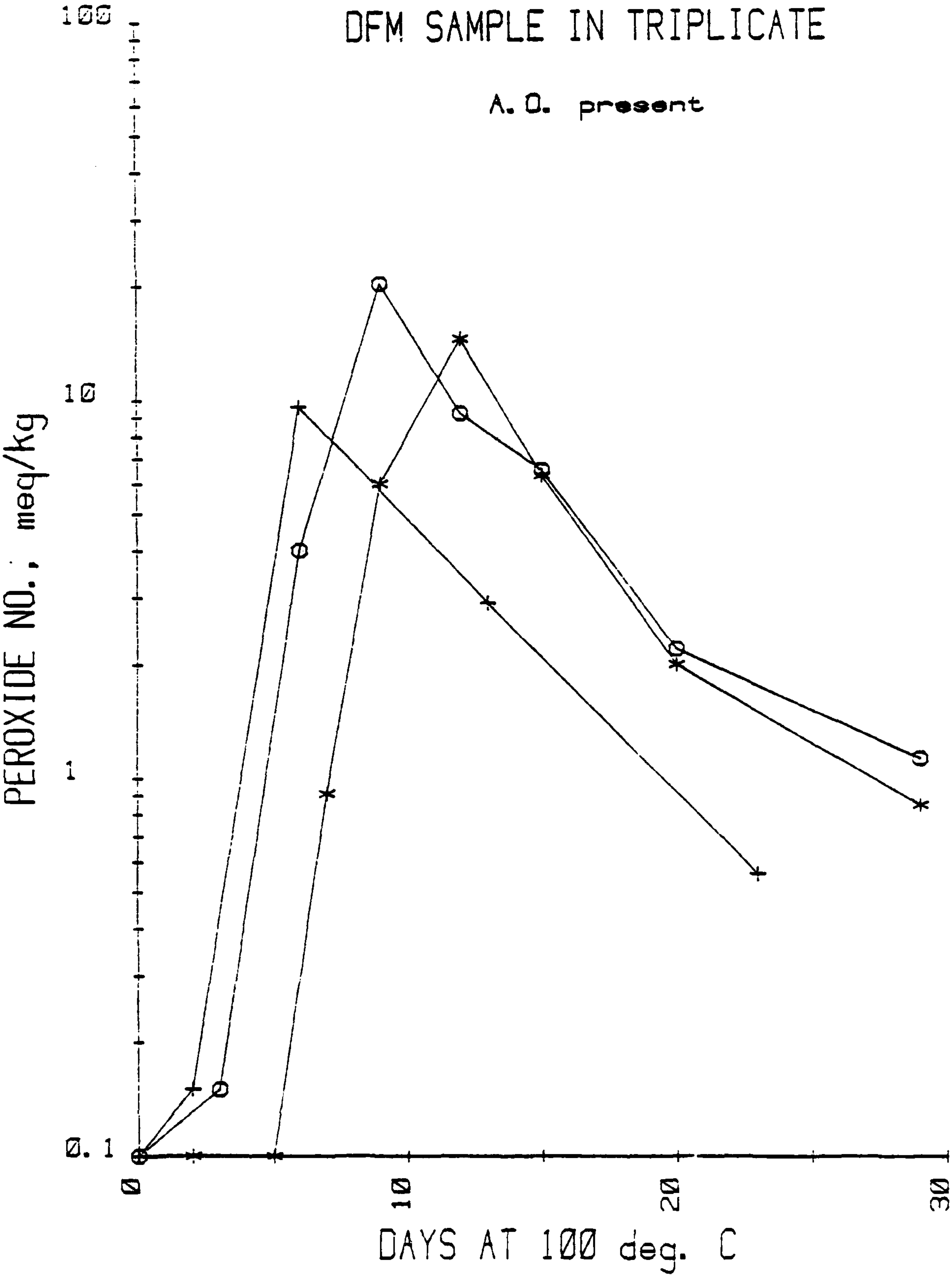
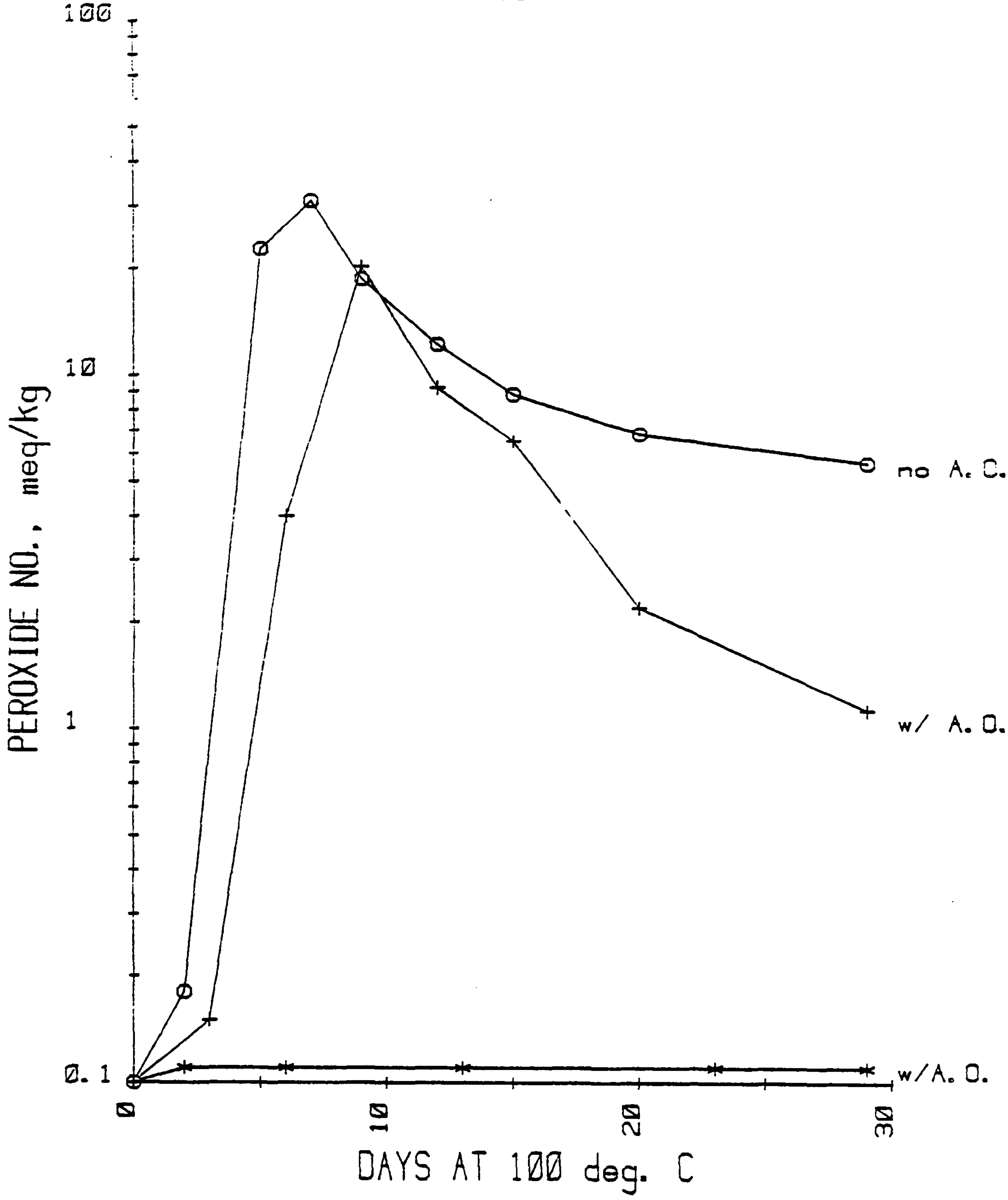


Fig. 6. PEROXIDATION OF 3 DFM SAMPLES FROM SHALE II



APPENDIX C

DETAILED RESULTS OF COOPERATIVE TEST PROGRAM 1

TABLE C-1

RESULTS OF COOPERATIVE TEST PROGRAM

	PEROXIDE NUMBER, MEQ/KG						
	HOURS AT 100°C						
LAB	3	7	24	48	72	96	168
	FUEL #1 - J22 (Shale) (JP-5) (with A.O.)						
WPAFB	.16	.20	2.09	3.18	12.69	3.98	1.30
	---	---	3.43	3.09	12.06	3.34	1.05
P & W	.89	1.13	1.82	2.87	3.89	6.42	13.20
	.85	1.07	1.91	2.72	3.68	6.70	13.83
SWRI	.70	.75	1.48	2.19	3.82	8.12	5.62
	.71	.64	1.64	2.42	4.74	7.98	3.25
NRL	.83	1.06	2.54	8.48	24.82	23.23	1.16
	.87	1.03	2.78	9.73	21.78	15.80	.62
	FUEL #2 - JP-5 (no A.O.)						
WPAFB	0	.19	3.99	2.96	18.50	23.60	16.35
	---	---	3.87	2.95	14.85	22.98	16.45
NAPC	1.30	5.97	21.89	32.93	49.26	42.48	49.94
	1.46	6.29	22.83	34.45	48.32	46.75	136.07
SwRI	.004	.09	4.07	15.23	29.47	---	60.42
	.006	.51	8.15	9.40	19.76	32.14	65.70
NRL	1.86	5.48	22.55	45.55	59.92	67.01	60.50
	1.36	5.56	26.63	50.44	73.55	76.85	57.51
	FUEL #3 - JP-5 (with A.O)						
WPAFB	---	.25	.70	3.24	3.19	.52	.20
	.40	.24	1.29	2.96	2.87	.66	.36
NAPC	0	0	.23	2.02	24.97	54.38	57.86
	0	0	.21	2.41	27.44	45.07	69.98
TEXACO	---	0	.10	.26	.46	1.00	23.59
	---	0	.08	.26	.48	.94	25.31
NRL	0	0	0	.26	.57	1.62	42.88
	0	0	0	.31	.98	2.99	43.12

TABLE C-1
(Continued)

	PEROXIDE NUMBER, MEQ/KG						
	HOURS AT 100°C						
LAB	3	7	24	48	72	96	168
			FUEL #4 - JET A (no A.O.)				
WPAFB	.21	.21	.57	3.10	3.10	2.82	12.62
	---	.20	.59	3.29	2.84	1.81	13.07
NAPC	0	0	.12	5.19	18.54	21.51	37.44
	0	0	.14	5.51	24.33	18.23	58.78
TEXACO	---	0	0	.31	1.03	5.39	25.66
	---	0	0	.28	1.27	6.33	27.04
SwRI	.002	0	.03	.11	.68	3.13	11.77
	.01	0	.02	.05	.30	1.07	13.45
WPAFB	.53	.40	.41	.06	---	.20	.51
	.49	.49	.34	.01	---	.21	.71
NAPC	0	0	.32	.61	.45	.30	.26
	0	0	.32	.47	.28	.39	.33
TEXACO	---	.25	.21	.51	.54	.56	.50
	---	.25	.24	.44	.52	.55	.55
P&W	.11	.10	.21	.31	.50	.89	1.48
	.13	.18	.25	.45	.57	.93	1.56
NRL	.02	.09	.22	.23	.22	.26	.21
	.11	.10	.22	.23	.22	.25	.22
			FUEL #6 - JP-5 IA (with A.O.)				
TEXACO	---	0	0	.30	.86	2.32	30.33
	---	0	0	.33	.79	2.15	28.44
P&W	0	0	.09	.30	.51	1.93	4.53
	0	0	.17	.34	.55	1.98	4.72
SWRI	.02	0	.03	.10	.26	.86	32.40
	0	0	.03	.10	.20	.84	30.97
NRL	0	0	0	.64	2.88	16.55	44.00
	0	0	0	.42	1.50	12.11	45.86

TABLE C-I
(Continued)

	PEROXIDE NUMBER, MEQ/KG						
	HOURS AT 100°C						
LAB	3	7	24	48	72	96	168
			FUEL #7 - JP-5 IB (no A.O.)				
P&W	.13	.21	6.40	12.96	21.15	22.84	24.92
	.10	.13	5.90	13.76	19.13	24.75	26.06
SWRI	.02	.23	9.08	17.82	23.00	40.04	53.88
	.04	.24	9.01	17.80	22.65	39.18	54.03
NRL	1.50	6.27	27.27	44.78	68.23	73.67	55.82
	1.30	5.57	21.61	35.41	55.82	59.18	51.65

TABLE C-II

AVERAGE % DIFFERENCE BETWEEN DUPLICATES

	FUELS							
LAB	1	2	3	4	5	6	7	LAB AVERAGE
A	19	6	28	12	17			16
B		6	17	23	25			18
C	5				15	7	7	9
D			8	13	7	8		9
E	19	40		61		8	2	26
F	22	14	33		3	35	17	21
FUEL AVER.	16	17	22	27	13	15	9	GRAND. AVER. = 17%

APPENDIX D

REPORT TO CRC
HYDROPEROXIDE TESTS AT FOUR TEMPERATURES

6180-444:RNH:cak
April 27, 1983

MEMORANDUM

To: CRC Panel and Test Participants on Jet Fuel Hydroperoxide Potential

From: Chairman

NRL has completed testing of four jet fuels for hydroperoxide potential at four temperatures (Encl. (1)). We are proposing a new test program for the CRC Panel to be conducted at a lower temperature than the 100°C used in the 1982 cooperative program. The proposed program will be discussed at the Panel meeting in Dayton, Ohio, May 9, 1:00 p.m.

Please consider offering fuel samples for the cooperative tests and proposing suggestions for improving the 1982 testing.

Bob Hazlett
R. N. Hazlett

Encl: NRL Test Results

REPORT TO CRC

NRL Hydroperoxide Tests at Four Temperatures

At the meeting of the CRC Hydroperoxide-Potential-of-Jet-Fuels Panel on April 19, 1982 a plan to develop an accelerated test by means of a cooperative test program was adopted. This program was completed last year. Results were collected and analyzed by NRL and reported to the CRC and the participants and also the Middle Distillate Fuel Stability Conference held at NRL October 27-28, 1982. In this program, seven jet fuels were stressed at 100°C for periods up to one week at six laboratories. At the October 27 meeting of the Hydroperoxide Panel, validity of the test temperature was discussed. To define the test temperature effect, NRL agreed to repeat the prior tests at lower temperatures, viz., 43°, 65° and 80°, using four of the same fuels. Storage times selected for the lower temperatures were selected in an attempt to find ones equivalent to the times used at 100°C (3,7,24,48,72,96 and 168 hours).

These tests were completed recently and are reported herewith. See Table A and Figures 1-5. The 100°C data were taken from the previous report. The time periods used were calculated according to the Arrhenius relation, namely doubling (or halving) of reaction rate for a 10°C change of temperature, and were then modified somewhat based on experience. Thus time factors of 30:1 and 10:1 were used for 43° and 65° tests instead of the calculated values of 52:1 and 11.3:1. Note that columns in the Table and horizontal scales of the graphs are labeled "equivalent hours at 100°C". The actual storage times at the several temperatures are shown at the end of the data table. Note also that the vertical scale of the several semi-log plots varies by two orders of magnitude. A linear plot for one fuel is also included.

The graphs reveal appreciable variation in peroxide number as a function of time, temperature and fuel. In the case of two fuels - Exxon Benicia JP-5 w/o AO and JP-4 w/o AO - there was fair agreement between the several temperatures based on equivalent time periods. Also, in at least two cases out of the four (Benicia JP-5 w/AO and JP-4 w/o AO), peroxide level at all times was lower at the lower tempertures. With two fuels out of four, results at the lower test temperatures were quite different from results at the higher temperatures - and hence not predictable from the latter. Thus, accelerated fuel stability tests at 80°C or 100°C may not be useful guides to storage stability at ordinary temperatures. This leads to a proposal to repeat the 100° round robin at a lower temperature.

Therefore, NRL proposes a follow-on cooperative test program with storage at 65° for a period of 10 weeks or 70 days. It is expected that there will be 5 fuels and 7 laboratories. The following have agreed to participate: NRL, WPAFB, P&WA, NAPC, SWRI, Texaco and duPont. More attention will be paid to various details to improve accuracy and precision. Ten gallons of each fuel instead of five will be procured in order to rinse the sample cans more thoroughly. Degree of exposure to the atmosphere may need controlling. Also container cleaning procedure may need to be tightened and oven thermometers must be calibrated. Another aid to improved precision could be a practice session for each analyst before starting the program but using a fuel other than one of the test fuels.

James M. Hall

James M. Hall

Bob Hazlett

Robert N. Hazlett

TABLE A

Fuel	Temp. °C	Time Factor	Average Peroxide No., meg/kg* Equivalent Hours at 100°C: 3	7	24	48	72	96	168
I J-22	43	30:1	-	-	1.03	1.10	1.38	1.74	2.66
w/A.O.	65	10:1	-	-	1.45	1.80	2.44	3.90	8.69
	80	4:1	-	1.10	2.53	7.43	18.4	43.3	1.48
	100	1:1	.85	1.05	2.66	9.11	23.3	19.5	0.96
II Benicia	43	30:1	-	-	13.2	41.0	82.5	111.0	133.0
w/o A.O.	65	10:1	-	-	13.5	53.3	86.3	121.1	198.0
	80	4:1	-	7.41	34.3	60.7	82.4	95.2	78.9
	100	1:1	1.61	5.52	24.6	48.0	66.8	72.0	61.5
III Benicia	43	30:1	-	-	0	0	0	0	0
w A.O.	65	10:1	-	-	0	0	0	0	.12
	80	4:1	-	0	0	.10	.16	.35	39.7
	100	1:1	0	0	0	.29	.78	2.31	42.9
V JP-4	43	30:1	-	-	.07	.03	.12	.14	.19
w/o A.O.	65	10:1	-	-	.10	.16	.12	.16	.14
	80	4:1	-	0	.24	.26	.25	.20	.30
	100	1:1	.07	.10	.22	.23	.22	.26	.22
			ACTUAL STORAGE TIMES						
	43		3.8d	8.8d	30d	60d	90d	120d	210d
All	65		30h	70h	10d	20d	30d	40d	70d
Fuels	80		12h	28h	4d	8d	12d	16d	28d
	100		3h	7h	24h	48h	72h	96h	168h

FIGURE D-1

J22 WITH ANTIOXIDANT

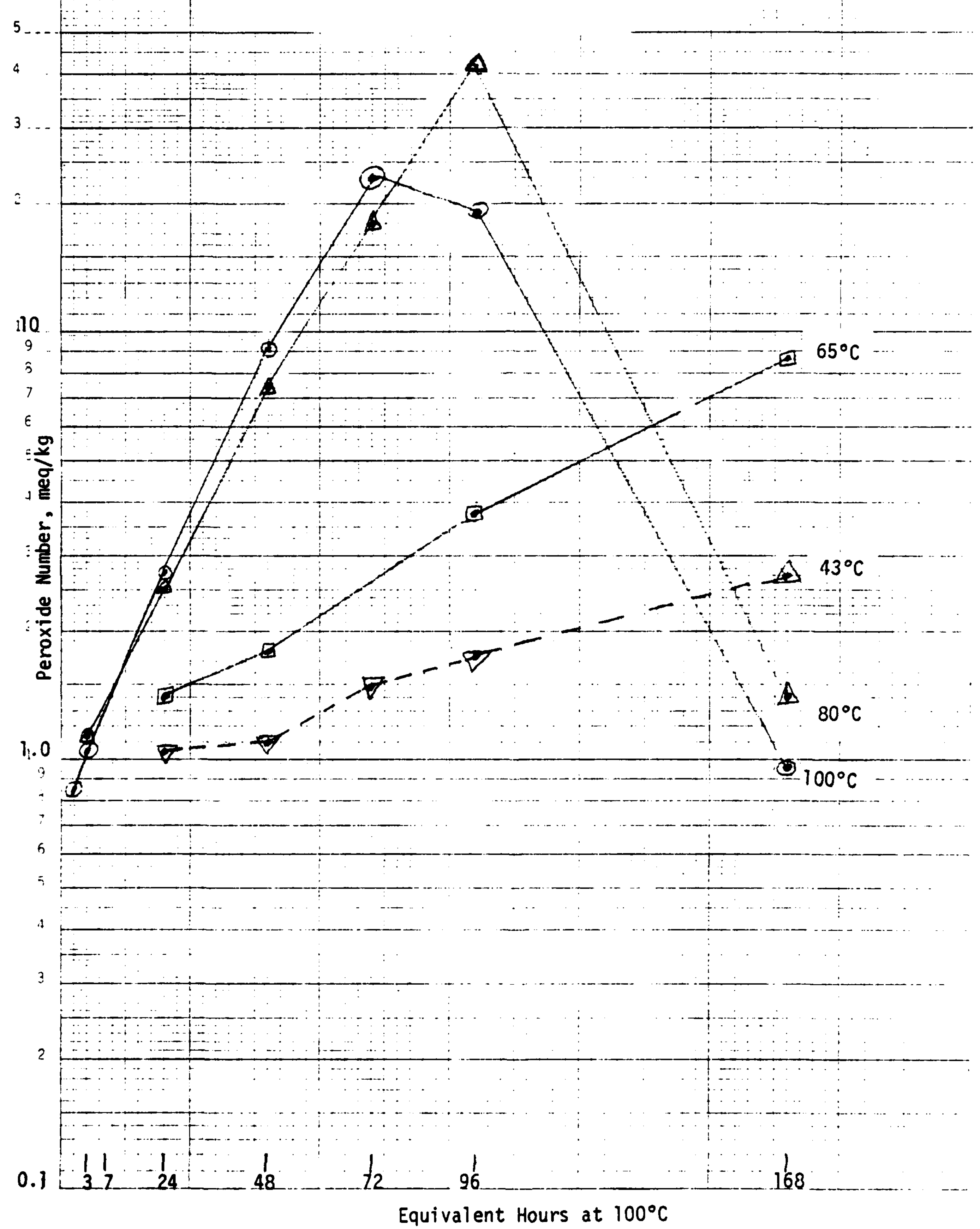


FIGURE D-2

BENICIA JP-5 WITHOUT ANTIOXIDANT

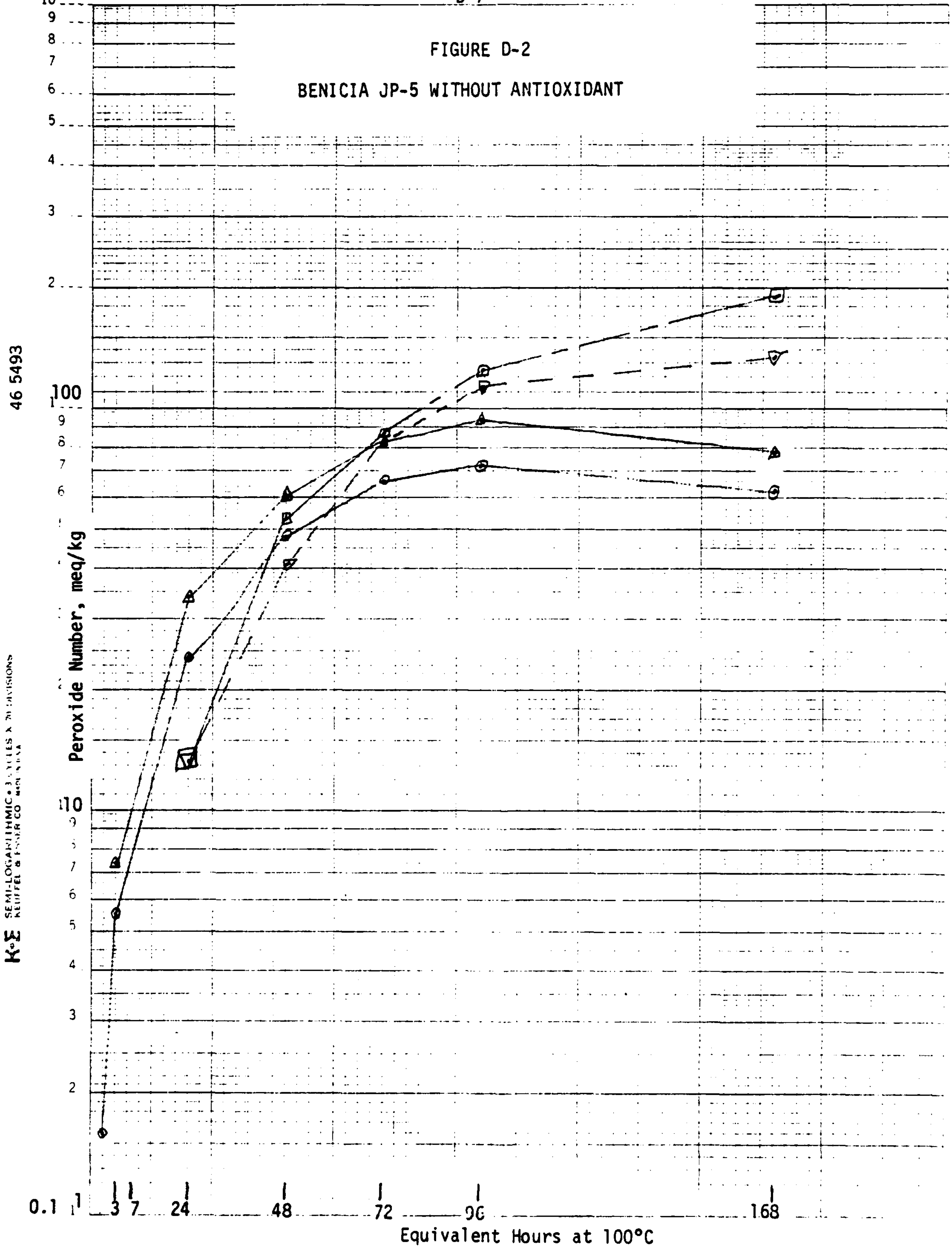


FIGURE D-3

BENICIA JP-5 WITHOUT ANTIOXIDANT

(Linear Plot)

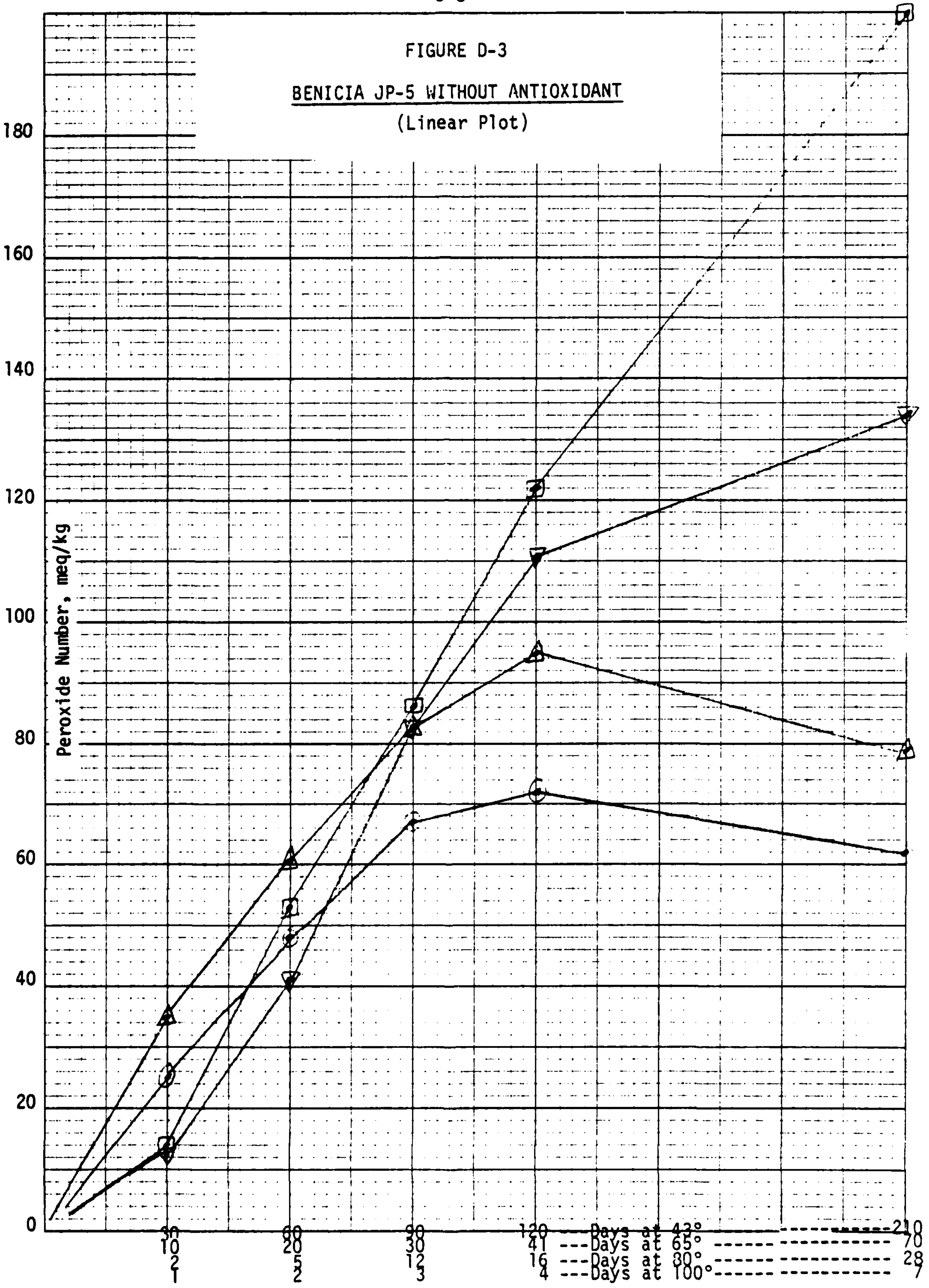


FIGURE D-4

BENICIA JP-5 WITH ANTIOXIDANT

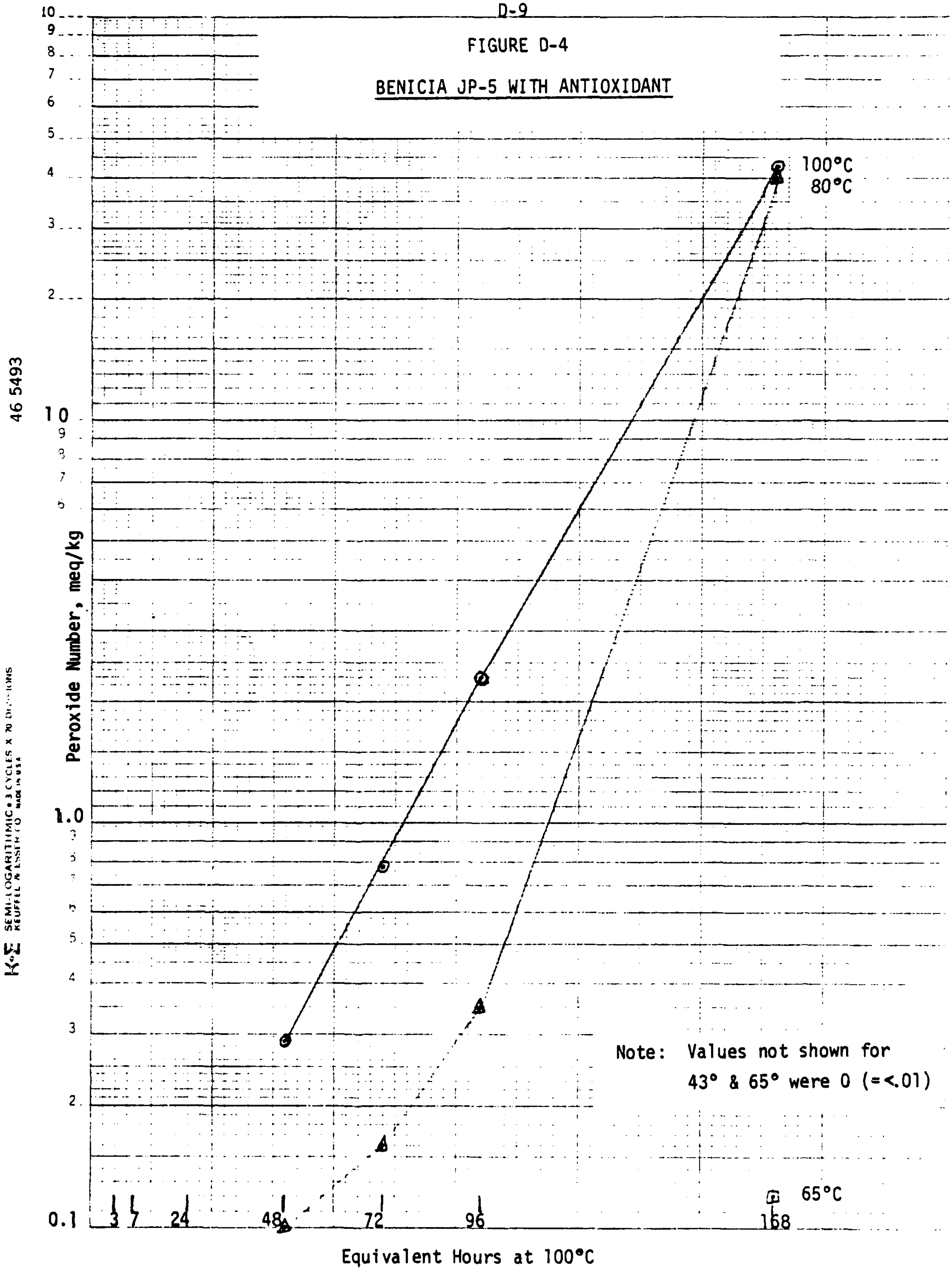
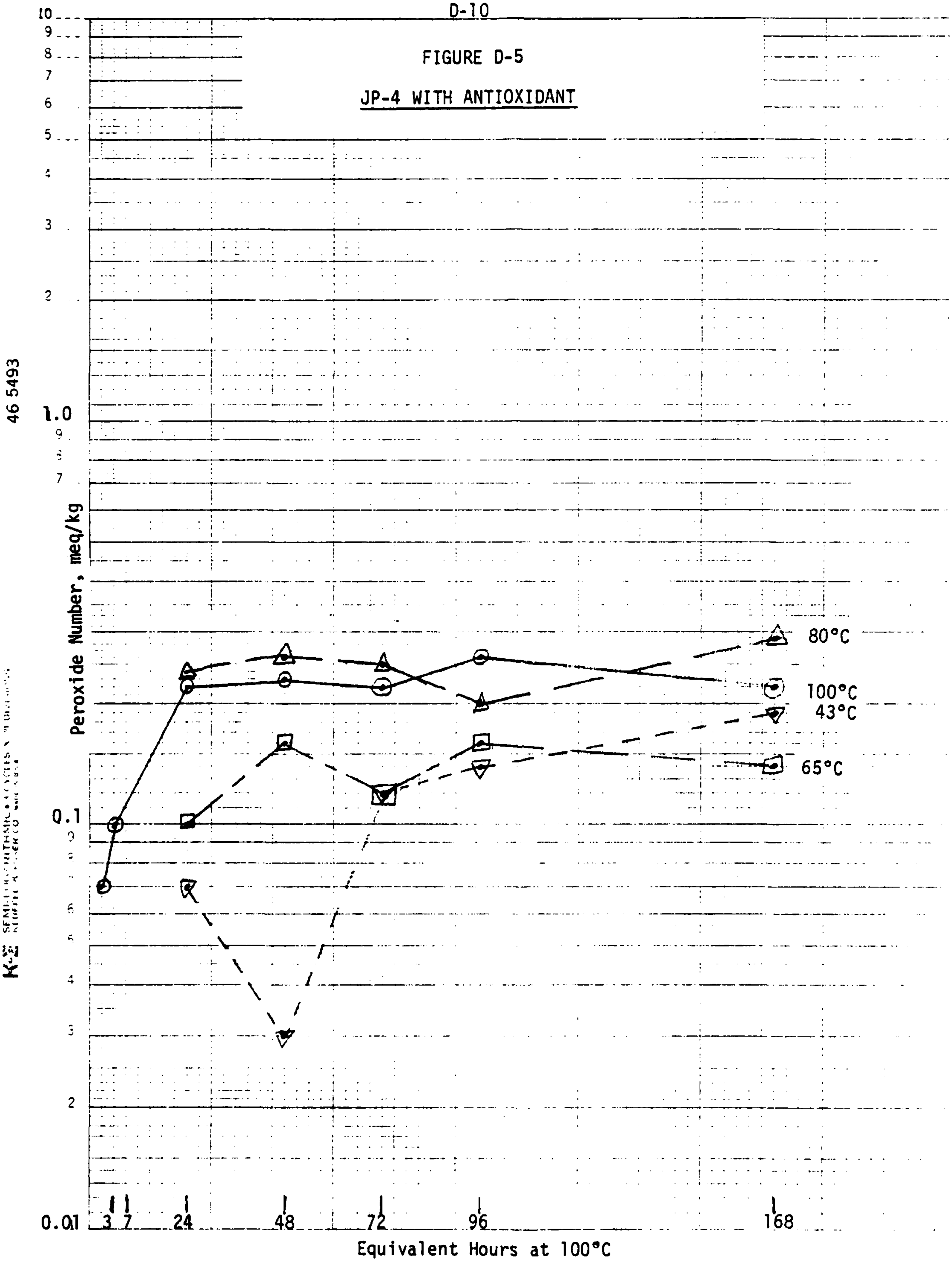


FIGURE D-5

JP-4 WITH ANTIOXIDANT



APPENDIX E

INSTRUCTIONS FOR THE SECOND COOPERATIVE TEST PROGRAM

DEPARTMENT OF THE NAVY
NAVAL RESEARCH LABORATORY
WASHINGTON, D.C. 20375

IN REPLY REFER TO:
6180-744:JMH:cak
October 19, 1983

To: Participants in the Second CRC Cooperative Test Program on Hydroperoxide Potential of Jet Fuels

From: J. M. Hall and R. N. Hazlett, Chemistry Division, Code 6180, Naval Research Laboratory, Washington, D. C. 20375

Introduction

At the CRC meeting May 9, 1983 at Dayton, Ohio, it was proposed to the Hydroperoxide-Potential-of-Jet-Fuels Panel that a second cooperative test program be conducted. The proposed program would be an accelerated test based on 65°C rather than the 100°C previously used. Possible sources of error and measures to reduce variability of results were discussed. Such sources are thought to include trace contamination, oxygen level, and oven temperature control. This program is scheduled for January next year to avoid shipment of samples during hot weather. The following outlines the proposed plan and procedures to reduce the excessive variability of results found in the 1982 program. The precautions and extra care noted below will occasion additional work but they are necessary for a successful outcome.

Background

Under the auspices of the CRC Panel on Hydroperoxide Potential of Jet Fuel, a cooperative test program was carried out by 6 laboratories in summer 1982 to develop an accelerated test for hydroperoxide potential. Seven samples of different jet fuels distributed to each participating laboratory were stored at

100°C for 168 hours with portions removed at intervals for hydroperoxide analysis. As you know, results were not altogether acceptable. In many cases there were very wide variations in peroxide number between laboratories for a particular fuel and time. The agreement between duplicate bottles, i.e., the "within laboratory" variation, was reasonably good, averaging 17%. However, the range was 2-61% and 20% of the results showed a difference between duplicate bottles of more than 25%. The 17% average difference between bottles is three times as high as the average difference between duplicate analyses as experienced at NRL.

NRL then conducted similar tests on four of the fuels at 43°, 65° and 80°C. Periods equivalent to those used at 100°C were calculated based on the Arrhenius law (reaction rates doubled or halved per 10°C difference) with minor adjustment based on experience. With two fuels there was fair agreement between the four temperatures based on equivalent time periods. In the case of the other two fuels, which contained anti-oxidant, namely, Shale J-22 and Benicia, there was wide divergence. Thus it appears that an accelerated test at 100°C or 80°C may not be predictive of behavior at lower temperatures, including ordinary fuel storage conditions.

Proposed Test Plan

The Plan follows closely the prior 1982 test plan but with the addition of procedural improvements to reduce variability of the results.

1. Test Fuels

	Sample	Source	Hydrotreatment	Antioxidant
1.	Benicia JP-5	Exxon	Severe	No
2.	Benicia JP-5	Exxon	Severe	Yes
3.	Shale JP-4	Air Force (Caribou)	Severe	No
4.	Shale JP-4	Air Force (Caribou)	Severe	Yes
5.	Jet A	Suntech	Moderate	No

These fuels will be shipped to NRL in 10-gallon amounts to permit more thorough rinsing of containers. NRL will transfer samples to clean one-gallon epoxy-lined cans and ship under nitrogen to the participants. Each laboratory will test each fuel in duplicate.

Oxygen content plays a role in the development of hydroperoxides in stored fuels. To standardize this factor, fuels will be purged with nitrogen and shipped under nitrogen. Each laboratory should then saturate all fuels with air just before starting stress testing. (Note this in report). Aerate by bubbling air through samples in the 500 ml bottles for 5 minutes at a moderate rate. In addition, at each sampling time leave cap off bottle for 15-30 minutes to permit replenishment of air.

Fuel samples should be stored at 30-40°F from time of receipt until beginning of storage.

2. Participating Laboratories

NRL	R. N. Hazlett & J. M. Hall
WPAPB	Bob Morris
NAPC	Lynda Craig
SWRI	Charles Rodriguez
P & W (Florida)	Bill Purvis
Texaco	M. A. Caggiano
Dupont	Cy Henry
[illegible]	[illegible]

3. Test Temperature - Stress fuels at 65°C ± 1°C

4. Sampling Times - 0 hour, 24 hr, 72 hr, 168 hr; 14, 21, 35 and 56 days

While pipets are convenient for transferring to the titration flask, each sample must be weighed. The amount of sample taken should be adjusted to the level of peroxides starting with 25-50 g. If a delay before analysis is unavoidable, store weighed samples in a refrigerator temporarily.

5. Samples - Place 400 ml of each fuel in each of two 500 ml sample bottles. Aerate before starting and at each sampling time as described above.

6. Special Calibration Samples -As a check on interlaboratory analytical bias or systematic error, a special fuel sample containing about 3 meq/kg of a stable hydroperoxide (e.g., t-butyl hydroperoxide) will be supplied. Keep in refrigerator except when sampling. This sample

should be run in quadruplicate and all results reported. This is designed to provide valuable data on laboratories' biases using an unchanging sample. It is recommended that this be done to coincide with the 14 day sampling time. Please report how this was done. If possible, do a second set of quadruplicate analyses at the 35 day sampling time.

7. Sample Bottles - 500 ml brown borosilicate bottles with caps with Teflon liners. Recommended source: Wheaton Scientific Co., 1000 North Tenth Street, Millville, N.J. 08332, (609) 825-1400, catalog No. 219689 Type 500, 24 bottles per case, w/o caps. Caps #240480, size 33-430, 100 per case. The above are also available from PGC Scientific, 9161 Industrial Court, Gaithersburg, MD 20760, (301) 840-1111 or American Scientific Products, 8855 McGaw Road, Columbia, Md. 21045, (301) 997-3400. If brown bottles are not used, wrap with foil.

Clean bottles and caps before use as directed below.

8. Oven - An explosion-proof oven with forced air circulation is recommended. State type of oven used in report. Thermometers and/or thermocouples (use at least two) must be calibrated. In case a forced draft oven is not used, check temperature further by monitoring a bottle of water or fuel appropriately placed in oven. On removing bottles from oven for sampling, cool them, e.g., in a hood draft or water bath, before opening.

9. Analysis - By ASTM D3703 except for the substitution of Freon 113 (1,1,2-trichlorotrifluoroethane) for carbon tetrachloride. Source: Miller-Stephenson, Inc. or Burdick and Jackson Laboratories, Inc. (Note that in NRL experience the use of Freon 113 in lieu of CCl_4 causes results to be 5-20% lower with fuels.) For further information see "The Determination of Organic Peroxides" by Johnson and Siddiqi, Pergamon Press 1970.

Normally 500 ml Erlenmeyer flasks are more convenient for titrations than 250 ml flasks.

The analyst, especially if unfamiliar with the analytical procedure, should practice on an in-house jet fuel before starting samples in the oven. The importance of such practice cannot be overemphasized. (To provide a fuel with an elevated P. N., heat a susceptible fuel or add a hydroperoxide.)

Observe the precautions noted in D3703. Reagents must be free of peroxides and dissolved oxygen. Boil the water used for dilution and for preparing the KI solution. Store the KI solution under chloroform or blanket with nitrogen. Prepare fresh often. Note: KI from some sources is unsuitable for iodometry. Run blanks before starting the program and at least occasionally during it. Use fresh $Na_2S_2O_3$.

Maximum cleanliness and precautions against contamination should be observed throughout. Clean all glassware scrupulously, especially the sample bottles and caps. Bottle and cap cleaning is described below. Do not use strong cleaning agents such as chromic acid.

(a) Fill bottle with high strength solution of laboratory detergent (Alconox made by Alconox Inc., NY, NY 10003 has been found suitable) in tap water, replace closure and allow to soak for at least 10 minutes.

(b) Vigorously scrub all bottle and closure surfaces with detergent solution.

(c) Repeatedly rinse bottle and closure with hot tap water until last tendency toward foam formation has disappeared.

(d) Generously wet closure and allow to soak for at least 10 minutes.

(e) Add hot tap water and repeat scrubbing and rinsing procedure until foaming tendency disappears.

(f) Rinse twice more with hot tap water.

(g) Fill with distilled water and let stand 1 hour.

(h) Rinse twice more with distilled water.

(i) Fill with acetone and let stand 1 hour.

(j) Rinse twice more with acetone.

(k) Rinse twice with toluene.

(l) Oven dry the bottle and closure separately at 120°C.

(m) After cooling, replace closure and store in clean laboratory until start of test.

(n) One or two days before start of test, fill bottle with fuel to be tested, close, shake thoroughly and let stand at least overnight.

(o) Rinse twice with test fuel immediately before adding 400 ml sample to bottle at start of stress.

Calculate peroxide number as milliequivalents of active oxygen per kilogram of sample (equal to 1/8 the P. N. in ppm as calculated by D3703). Report all results, not just averages. This is necessary for statistical evaluation. Do not round off data. Do not discard an analytical result solely because it seems to differ too much from the duplicate bottle or from the expected value. <u>In case results for any pair of duplicate bottles differ by more than 15-20%, repeat both analyses and report all four results.</u>

Randonmize procedure whereever possible. For example, at the several sampling times vary the order of analyzing fuels and duplicate bottles. Avoid running duplicate bottles in succession.

Send results to Panel Chairman.

10. <u>Miscellaneous</u> - Report any unusual observations.

11. <u>Other Tests</u> - Some monitoring of acid number and also sediment formation is desirable. Fluorosilicone O-rings

used in aircraft fuel systems are subject to deterioration by acids. Volunteers are hereby solicited for one or both analyses. Procedures: (a) Acid No. ASTM D3242, 65°C, 21 and 56 days, 2 bottles, separate from peroxide tests; (b) Sediment Formation - procedure to be supplied by NRL, 65°C, 56 days, 2 bottles, 1 test each.

It is also desirable in this program to obtain peroxide data at temperatures other than 65°C. Again, volunteers please. This would involve duplicating the 65° tests at 43°, 80° and 100°C. Sampling times would be the 65° values times the factors 4, 1/3 and 1/10 respectively.

R. N. Hazlett

R. N. Hazlett, Head
Combustion & Fuels Branch
Chemistry Division

J. M. Hall

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APPENDIX F

DETAILED RESULTS OF COOPERATIVE TEST PROGRAM 2

DEPARTMENT OF THE NAVY
NAVAL RESEARCH LABORATORY
WASHINGTON, D.C. 20375

IN REPLY REFER TO:

6180-1084:JMH:cem
29 October 1984

From: R.N. Hazlett, Chairman, CRC Hydroperoxide-Potential-of-Jet-Fuels Panel

To: Participants in the Second CRC Cooperative Test Program on Hydroperoxide Potential of Jet Fuels
(DISTRIBUTION LIST ATTACHED)

Subj: RESULTS OF SECOND COOPERATIVE TEST PROGRAM

Encl: (1) Two copies of subject report
(2) Distribution List

Enclosed is a compilation of results for the recently completed Round Robin II on jet fuel hydroperoxide potential. I wish to extend thanks to you and your organizations for your efforts in carrying out this work. Hopefully, it will lead to an improved method for evaluating fuels of the future.

In addition, on behalf of the Hydroperoxide Panel, I wish to thank Bill Dukek and Bob Morris for supplying fuel samples.

Due to my imminent departure for a year's assignment in Australia, I have resigned as chairman of the CRC Hydroperoxide Panel. The succeeding chairman will be named by Bill Taylor of Exxon R&E Co.

If you have any questions on the enclosed results, please call Jim Hall at 202/767-2673.

Dennis Hardy for RNH

ROBERT N. HAZLETT
DENNIS HARDY, Acting Head
Fuels Section
Combustion & Fuels Branch
Chemistry Division

DEPARTMENT OF THE NAVY
NAVAL RESEARCH LABORATORY
WASHINGTON, D.C. 20375-5000

IN REPLY REFER TO:
6180-616-DRH:cem
12 June 1985

From: Dennis Hardy, Fuels Section, Chemistry Division, Naval Research Laboratory

To: Participants in the Second CRC Cooperative Test Program on Hydroperoxide Potential of Jet Fuels

Subj: Correction to "Results of the Test Program", dated 5 October 1984 and distributed to participants 29 October 1984

Paragraph "4a" on page 1 is in error. It should read: "Variability of the analytical procedure is shown by the 10 cases of duplicated analyses (1 case each in Fuels 2 and 4 and 8 cases in Fuel 3). The average percent difference between duplicate analyses was 13% and the range was 1-50%. Individual values were 14 (Fuel 2), 2, 45, 42, 5, 21, 1, 3, 3 and 17% (Fuel 4) for the first sample and 4 (Fuel 2), 7, 50, 7, 1, 18, 2, 1, 1 and 7% (Fuel 4) for the second sample." The underlined values are the changes or additions.

Also the value "00.0" shown in Table 3, Fuel 3 for P&W at 56 days should be 100.0 and the value ".3" for Tex at 3 days should be .36.

If you have any questions, please call James Hall at 202/767-2673.

DENNIS HARDY, Acting Head
Fuels Section
Combustion & Fuels Branch
Chemistry Division

6180-1084A:JMH:cem
5 October 1984

Subj: RESULTS OF THE SECOND CRC COOPERATIVE TEST PROGRAM ON HYDROPEROXIDE POTENTIAL OF JET FUELS

1. The second cooperative hydroperoxide test program was carried out under CRC auspices to investigate further the development of an accelerated test for hydroperoxide potential of jet fuels using for analysis ASTM D3703-78 ("Standard Test Method For Peroxide Number of Aviation Turbine Fuels"). This work is of interest especially for hydrotreated fuels and fuels from non-petroleum sources. In the first test program, which was carried out in 1982 by six laboratories, selected fuels were stored at 100°C for 7 days and analyzed periodically for peroxides. Results showed wide variations between laboratories and between duplicate samples. These results plus subsequent work at NRL at 43°, 65° and 80°C indicated that an accelerated test at 80° or 100°C is not predictive of behavior at lower temperatures, including ordinary fuel storage conditions.

2. For the second test program, fuels were stored at 65°C for 56 days and procedures were improved and tightened to reduce excessive variability of results. Please refer to the 9-page set of directions sent to each participant by NRL October 19, 1983.

3. Results from the second test program are summarized below. Table 1 lists for reference the laboratories and personnel involved. Table 2 identifies the fuel samples supplied to the laboratories. Unfortunately, two planned fuels were not available and the substitutes were less appropriate (too stable). Final peroxide numbers of about 1 and greater were desired.

4. Results are shown in Table 3. For each lab the two horizontal lines represent the two duplicate samples of each fuel. Only Fuel 3 developed appreciable hydroperoxides. None of the other four fuels reached a peroxide number of 1. Repeatability and reproducibility may be summarized as follows:

a) Variability of the analytical procedure is shown by the 8 cases of duplicated analyses.* The average percent difference between duplicate analyses was 8% and the range was 1-21% except for one case of 42%. Individual values were 13, 2, 42, 5, 21, 1, 3 and 3% for the first sample and 4, 7, 7, 1, 18, 2, 1 and 1% for the second sample.

b) Agreement between the duplicate samples of any one fuel was usually within 25% but varied from 0 to over 50%. Individual values are given in Table 4. These are quite variable and

*Note - Where the two samples differed by more than 15-20%, labs were instructed to repeat the analysis and report the four results.

unpredictable. They represent analytical variability plus any variability between individual paired samples. It is obvious in some cases that differences between originally identical samples did develop on aging at 65°C. Thus fuel behavior toward peroxidation (at elevated temperature) is variable and hence predictable only to a limited degree. This agrees with prior experience.

c) Agreement between laboratories was fair to poor. For peroxide numbers below 1, the range or spread was typically about 3 to 1.** SWRI's results for Fuel 5 at 35 and 56 days were abnormally (?) high so that the range for those times was over 10 to 1 instead of 3 to 1 otherwise. In the case of Fuel 3 the ratio of the high lab to the low lab was over 20 to 1 at 56 days. Thus repoducibility was perhaps no better than in Round Robin I in spite of added precautions.

5. Results of analyses of a "control sample" are shown in Table 5. The average of each set of quadruplicate (or duplicate) analyses is included, and also the ratio of the spread to the mean (as a percent). This sample was a dilute solution of a pure stable hydroperoxide in a solvent stable to peroxidation. It was held at low temperature except during shipping. The purpose here was to obtain better data on the analytical repeatability (within labs) and the reproducibility (between labs) using a stable sample free from (a) the complexity of having a mixture of peroxides of different types and (b) changes due to accelerated storage. The average of the values for percent spread (the "immediate" repeatability) was 6.2% and the range of these values was 0.2 to 15.4%. The 6.2% may be compared roughly to the 8% above. "Non-immediate" repeatability* <u>in the worst case for each lab</u> was as follows:

NRL	2%
P&W	5
Dupont	17
SWRI	1
TEXACO	7

Agreement between labs may be shown by aggregated averages for each lab (since there were no trends with time):

NRL	10.17
NAPC	10.12
P&W	9.93
Dupont	10.51
SWRI	9.53
TEXACO	9.20
	9.91

The spread here is 13%.

---
* I.e., comparing averages for different times.

** (Ratio of highest value to lowest value)

6. To summarize, these data are somewhat encouraging and perhaps the best data yet on the underlying repeatability and reproducibility of the analytical method, ASTM D3703. But application to jet fuels introduces additional variability inherent in the fuels. Accelerated testing of fuels then introduces further variability. A further purpose of the control sample was to calibrate the labs absolutely, assuming the control sample contained a known concentration of hydroperoxide (obtained other than by iodine titration). A sample of t-butyl hydroperoxide was specially vacuum distilled for this purpose. Its purity by gas chromatography was 99.6%. However, it was not available in time and the sample actually used did not have an accurately known purity.

Problems with the iodometric titration were encountered by several laboratories. For one thing, troubles were experienced with starch indicator solutions. At times on approaching an end-point, the color changed from purple to a dirty red to pale yellow. In such cases it is impossible to get a good end-point value, especially if the fuel itself is pale yellow. At times there was no color at all. Several brands or sources of starch in powder form and as prepared solutions were utilized, all with the same problems. At NRL we now prepare starch solution fresh daily.

Another problem involved the blank correction. Variabilty thereof might explain some of the variability of fuel results. Some tests at NRL showed that age of the starch solution was critical. In addition reaction time (see below) had a pronounced effect. For example:

Reaction Time	Blank, ml of .005N Na_2SO_3 Starch Solution: Fresh	Blank, ml of .005N Na_2SO_3 Starch Solution: 1-Day Old
5 min	0-0.2	0.2-1.6
30 min	--	0.8-2.9

7. The effect of reaction time has been studied at Pratt & Whitney and at NRL with a view to improving the repeatability of hydroperoxide analyses. Preliminary work indicated that higher peroxide numbers resulted when a longer reaction time was used. It was hoped that use of 10-15 minutes, for example, instead of 5 minutes would permit operation on a less steep part of the time curve. This was not borne out by further work at NRL. A statistically designed study of the effect of solvent (Freon 113 vs CCl_4) and reaction time (30 vs 5 minutes) was carried out using 3 fuels having initial peroxide numbers of 3-20 and standard $K_2Cr_2O_7$. Freon 113 was tested to support the change in procedure to that solvent in place of CCl_4. The use of Freon usually gave lower peroxide numbers but the differences were small (-7 to +6%) and not significant. The effect of 30-minute reaction time varied greatly with fuel type. Again no

significant effect could be supported statistically in view of the few data and the poor repeatability. Duplicates usually agreed within 10% but one fuel was much worse.

8. A further investigation compared results at 5, 10, 15, 30 and 45 minutes using Freon as solvent. Four fuels with initial peroxide numbers of 4-116 were utilized. Again the order of testing was randomized to enhance reliability of results and separation of variables (known and unknown). Resulting peroxide numbers were calculated relative to standard $K_2Cr_2O_7$ at the same reaction times rather than being expressed on an absolute basis. Generally, results were irregular and agreed poorly with previous data. The effect of reaction time varied widely with fuel type. In some cases the peroxide number rose irregularly (by up to 20%) with reaction time with a maximum at 15 or 30 minutes followed by a decline. Agreement of duplicates became worse with longer reaction times.

9. Paul Warner of Pratt & Whitney determined changes in fuel total acid number and fuel sediment formation after stressing at 65°C. Triplicate 300 ml aliquots of each fuel were taken for each type of test. Results are shown in Tables 6 and 7.

Table 1 - PARTICIPATING LABORATORIES

1.	NRL	Naval Research Laboratory	Jim Hall
2.	NAPC	Naval Air Propulsion Center	Linda Craig
3.	P&W	Pratt & Whitney Aircraft	Bill Purvis, Linda Neubauer
4.	Dupont	E.I. duPont de Nemours	Tayman Phillips
5.	TEX	Texaco, Inc.	Salvatore Rand
6.	SWRI	Southwest Research Institute	Pat Cuellar

Note - Wright Field (Bob Morris) and Exxon (Bill Dukek) have been unable to complete the test program.

Table 2 - TEST FUELS

Fuel No.	Type	Source	Hydrotreated	Anti-oxidant
1	JP-5	Andrews AFB	?	Yes?
2	Shale JP-4	Caribou via WPAFB	Severe	Yes
3	JP-5	Exxon Benicia	Mod. Severe	No
4	"	" "	" "	Yes
5	JP-4	Andrews AFB	?	?

Note - All petroleum-derived except Caribou

Table 3 - RESULTS OF 65°C TESTS

Peroxide Number, meq/kg

LAB	0	1	3	7	14	21	35	56
	Days Stressed at 65°C							
			FUEL 1 -- JP-5 (Andrews AFB)					
NRL	.00 .00	.00 .00	.00 .00	.00 .00	.00 .00	.00 .00	.00 .00	.01 .00
NAPC	.24 .18	.25 .23	.71 .70	.14 .17	.20 .19	.20 .21	.14 .12	.00 .00
P&W	.00 .00	.00 .00	.00 .00	.00 .00	.00 .00	.00 .00	.00 .00	.00 .00
Dupont	.00 .00	.00 .00	.00 .00	.00 .00	.00 .00	.00 .00	.00 .00	.00 .00
SWRI	.01 .01	.02 .02	.01 .02	.01 .03	.04 .03	.05 .04	.09 .08	.07 .07
TEX	.00 .00	.00 .00	.00 .00	.00 .00	.00 .00	.00 .00	.00 .00	.04 .03

Table 3 - (continued)

Peroxide Number, meq/kg

LAB	Days Stressed at 65°C 0	1	3	7	14	21	35	56
FUEL 2 - Shale JP-4 (Caribou)								
NRL	.00	.00	.00	.00	.00	.00	.17	.43
	.00	.00	.00	.00	.00	.00	.17	.48
NAPC	.00	.00	.00	.20	.14	.15	.26	.31
	.00	.00	.00	.19	.11	.11	.26	.45
P&W	.00	.00	.00	.00	.00	.00	.10	.31 .27
	.00	.00	.00	.00	.00	.00	.10	.24 .25
Dupont	.00	.00	.00	.04	.01	.06	.14	.30
	.00	.00	.00	.00	.02	.11	.16	.28
SWRI	.00	.00	.03	.07	.06	.06	.08	.17
	.00	.01	.02	.04	.05	.06	.08	.18
TEX	.00	.00	.00	.00	.00	.04	.08	.27
	.00	.00	.00	.00	.00	.04	.09	.24

Table 3 - (continued)

Peroxide Number, meq/kg

LAB	0	1	3	7	14	21	35	56
				Days Stressed at 65°C				
FUEL 3 - Benicia JP-5 w/o A.O.								
NRL	.00	-	.45	7.39	51.0 52.0	94.2	119.6	148.1
	.00	-	.33	7.14	36.2 38.9	88.5	99.5	124.2
NAPC	.00	.22	.21	1.58 1.00	27.6 42.5	75.5	142.4	323.5
	.00	.07	.18	1.80 1.08	22.2 23.8	70.0	156.0	285.0
P&W	.00	.00	.00	.74	24.8	55.4	78.8	89.7
	.00	.00	.00	.79	21.0	64.1	92.0	00.0
Dupont	.00	.12	1.03	9.70	26.3	32.5 34.2	41.3 51.2	63.5
	.00	.08	.80	9.10	26.3	22.5 22.7	31.7 37.9	37.5
SWRI	.00	.00	.16	.69	10.3	12.7	16.9	15.3
	.00	.03	.16	.73	10.3	12.6	17.0	15.3
TEX	.00	.06	.3	4.94	32.8	68.1 68.6	102.7 106.0	156.9 161.4
	.00	.06	.34	5.27	34.3	59.1 60.3	85.3 86.4	115.2 116.2

Table 3 - (continued)

Peroxide Number, meq/kg

LAB	0	1	3	7	14	21	35	56
	Days Stressed at 65°C							
FUEL 4 - Benicia JP-5 w/A.O.								
NRL	.00	.00	.00	.038	.126	.130	.215	.397
	.00	.00	.00	.049	.064	.186	.219	.372
NAPC	.00	.00	.00	.10	.16	.34	.27	.20
	.00	.00	.00	.13	.14	.27	.23	.29
P&W	.00	.00	.00	.00	.078	.104	.25	.49
	.00	.00	.00	.00	.070	.089	.20	.42
Dupont	.00	.00	.00	.07	.15	.22	.27 .32	.52
	.00	.00	.00	.09	.15	.20	.13 .14	.43
SWRI	.00	.00	.03	.05	.07	.11	.12	.15
	.00	.03	.03	.02	.06	.11	.13	.15
TEX	.00	.00	.00	.00	.04	.08	.15	.27
	.00	.00	.00	.00	.04	.07	.14	.25

Table 3 - (continued)

Peroxide Number, meq/kg

LAB	Days Stressed at 65°C: 0	1	3	7	14	21	35	56
FUEL 5 - JP-4 (Andrews AFB)								
NRL	.00	.00	.00	.00	.00	.00	.134	.175
	.00	.00	.00	.00	.026	.00	.075	.165
NAPC	.35	.37	.34	.26	.43	.45	.37	.44
	.36	.33	.31	.28	.45	.43	.45	.35
P&W	.00	.00	.00	.00	.079	.086	.10	.20
	.00	.00	.00	.00	.081	.084	.10	.20
Dupont	.02	.01	.01	.17	.13	.14	.13	.14
	.04	.03	.00	.10	.14	.12	.14	.14
SWRI	.02	.05	.07	.09	.18	.23	1.32	1.66
	.02	.04	.07	.11	.18	.21	1.30	1.61
TEX	.00	.00	.00	.02	.05	.07	.11	.21
	.00	.00	.00	.02	.05	.08	.13	.25

Table 4 - PERCENT DIFFERENCE BETWEEN DUPLICATE SAMPLES

Peroxide Number, meq/kg

LAB	0	1	3	7	14	21	35	56
				Days Stressed at 65°C				
				FUEL 1				
NAPC	29	8	1	19	5	5	15	-
				FUEL 2				
NRL							0	11
NAPC				5	24	31	0	37
P&W							0	25 8
Dupont						59	13	7
SWRI							0	6
TEX						0	12	12
				FUEL 3				
NRL			31	3	34 29	6	18	18
NAPC			15	13 4	22 56	8	9	13
P&W				7	17	15	15	11
Dupont		40	25	6	0	36 40	26 30	51
SWRI			0	6	0	1	1	0
TEX			6	6	4	14 13	19 20	31 33
				FUEL 4				
NRL				21	65	35	2	6
NAPC				26	13	23	16	37
P&W					11	15	22	15
Dupont				25	0	10	70 78	19
SWRI					15	0	8	0
TEX					0	13	7	8
				FUEL 5				
NRL							56	6
NAPC	3	11	9	7	5	5	20	23
P&W					5	2	0	0
Dupont				52	7	15	7	0
SWRI				20	0	9	2	3
TEX					0	13	16	17

Table 5 - CONTROL SAMPLE RESULTS (t-BuOOH in JP-5*)

Peroxide Number, meq/kg

LAB	Days Stored in Refrigerator† 0	3	7	14	16	21	35	56
NRL				10.30	10.08		10.12	10.16
				10.42	10.27		9.66	9.86
				9.80	10.18#		10.54	10.01
				9.87	1.9%		10.88	10.34
				10.10#			10.30#	10.09#
				6.1%			11.9%	4.8%
NAPC					10.10			
					10.78			
					9.74			
					9.22			
					10.77			
					10.12#			
					15.4%			
P&W				10.3			9.5	
				10.1			10.0	
				10.2			9.8	
				10.0			9.6	
				10.15#			9.7#	
				3.0%			5.2%	
Dupont	10.03	10.13	10.55	11.45		10.25	10.70	9.55
		10.10	11.20	11.20		10.48	10.95	9.53
		10.12#	10.88#	11.33#		10.37#	10.83#	9.54#
		0.3%	6.0%	2.2%		2.2%	2.3%	0.2%
SWRI				9.34			9.61	
				9.03			9.37	
				9.92			9.84	
				9.62			9.44	
				9.48#			9.57#	
				9.4%			4.9%	
TEX				9.13			9.36	
				9.00			9.33	
				8.87			9.81	
				8.55			9.54	
				8.89#			9.51#	
				6.6%			4.9%	

* Fuel 1

† Dupont stored at 40°C

\# The first value is the average and the second is the ratio of the spread to the mean as a percent.

Table 6 - TOTAL ACID NUMBER PER ASTM D3242

FUEL SAMPLES	BASELINE	21 DAYS	56 DAYS
1A	.006	.004	.004
1B	.005	.005	.005
1C	--	.005	.005
2A	.003	.004	.003
2B	.003	.003	.003
2C	--	.003	.003
3A	.001	.004	.023
3B	.001	.003	.018
3C	--	.004	.019
4A	.001	.001	.001
4B	.001	.001	.001
4C	--	.001	.001
5A	.003	.002	.002
5B	.003	.002	.002
5C	--	.002	.002

TABLE 7 - SEDIMENT FORMATION

FUEL SAMPLE	FILTERABLE SEDIMENT (g.)	ADHERENT GUM (g.)
1A	-0.0010	+0.01
1B	-0.0006	+0.03
1C	-0.0004	+0.05
2A	-0.0010	+0.01
2B	-0.0009	-0-
2C	-0.0008	+0.01
3A	+0.0002	+0.05
3B	+0.0007	+0.03
3C	+0.0001	-0-
4A	-0.0003	+0.01
4B	-0-	-0-
4C	-0.0005	+0.01
5A	+0.0002	+0.02
5B	+0.0003	+0.01

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APPENDIX G

INSTRUCTIONS FOR THE THIRD COOPERATIVE TEST PROGRAM

7 April 1986

To: Participants in the Third CRC Cooperative Test Program on Hydroperoxide Potential of Jet Fuels

From: J. M. Hall, Geo-Centers, Inc., at Naval Research Laboratory, Chemistry Division, Code 6180, Washington, D.C. 20375

Subject: Procedure for the Third CRC Test Program

Introduction

The test program for the third peroxide Round Robin will follow the previous plan in general. Please refer to the enclosed copy of our instructions dated 19 October 1983 to laboratories participating in the second round robin. A summary of procedure changes and additions for the third cooperative program is given next.

Changes For Round Robin III

1. The second round robin was unsatisfactory because of unsuitable fuels. Only one fuel developed a significant level of peroxide (>0.5 meq/kg). This time fuels have been selected which have been hydrotreated moderately or severely and which contain no antioxidant. Hence all were expected to develop hydroperoxides readily at 65°C. They have been screened at NRL.
2. There are 9 fuel samples and 9 laboratories instead of 5 fuels and 7 labs. This will permit superior statistical conclusions. Eight of the fuels are JP-5 and Jet A jet fuels and one is a JP-4 (fuel #5). 2000-2800 ml of each fuel is being supplied. The samples will be shipped under argon in new, epoxy-lined 1-gallon cans. These were cleaned twice with acetone with agitation, dried in a 43°C roomand rinsed with fuel, again with overnight soaking and agitation.
3. Set up 3 bottles (instead of 2) of each fuel. Place 400 ml of fuel in each bottle. This allows for 50 ml periodic samples for analysis in the beginning and for fuels developing only low levels of peroxide. Aerate all samples just before placing in the oven, as described below.

4. Sampling times: 0,1,2,3,4 and 6 weeks. Since 27 analyses (9 fuels x 3 bottles) are too many to handle in one day, it is suggested that half (or a third) be started in the oven on a Monday, for example, and the other half 1 or 2 days later. Do one analysis per bottle each time. Originally it was planned to limit the hot stress to 3 weeks but screening tests at NRL showed that several fuels developed significant hydroperoxide more slowly than expected.
5. Stress samples at 65±1°C in a forced draft oven as before.
6. Increase access to air as follows. Except for Fuel #5 (more volatile), screw caps on bottles loosely on putting in or returning to oven. As before, leave caps off bottles for 15-30 minutes at each sampling time.

Precautions

Sample cans should be stored in a refrigerator from time of receipt until start of heat stress. Tops of cans should be cleaned carefully before opening to prevent contamination. Just before putting in the oven, saturate fuels with air by bubbling clean, filtered air thru samples in the 500 ml bottles for 5 minutes at a moderate rate, e.g., 3 SCFH.

Start the test program by May 1 if possible.

Analyses

The analytical method is ASTM D3703-85, Peroxide Number of Aviation Turbine Fuels. (This includes the change to Freon 113 solvent as compared to the 1978 version.) Report peroxide number as meq/kg rather than as ppm.

If, at any time, the 3 bottles differ by more than 15%, repeat analyses on all 3 and report all six results. For cases of peroxide number below one, use 0.3 peroxide number instead of a percentage.

If the analyst is not accustomed to running the D3703 procedure, it is essential to practice before starting the program. Use actual jet fuel samples having both high and low peroxide levels. Samples can be provided by putting aerated fuel in a 100°C oven for 1 or 2 days or longer.

Control the 5-minute reaction time closely (±¼ minute or less). Results vary with reaction time and vary differently with different fuels.

Run blanks at least occasionally and report results.

It is very desirable to randomize the order of analyzing the samples. For example, don't titrate bottles of the same fuel in succession. Assuming the 27 bottles are divided into at least 2 groups and titrated on different days, divide each group of 3 among the 2 or 3 different weekdays.

There have been problems with starch indicator solution, e.g., strange end-point colors. Age is critical. We now avoid the problem by preparing fresh solution each day. It may be possible to use it a second day by reboiling before use.

Use deaerated distilled or deionized water to prepare reagents. Make fresh KI solution each day.

Calibration Sample

As before, a calibration or control sample will be provided, shipped separately. It will be a solution of t-butyl hydroperoxide in a very stable JP-5 with a peroxide number of about 3 meq/kg. Keep it in a refrigerator. DO NOT PUT IN OVEN. Analyze it twice in quadruplicate at, say, 1 and 3 weeks, or 2 and 4 weeks or similarly.

List of Participants

1. Naval Research Laboratory (Geo-Centers, Inc.)	J. M. Hall
2. Naval Air Propulsion Center	Lynda Turner
3. Wright-Patterson Air Force Base	Tim Dues
4. Southwest Research Institute	Pat Cuellar
5. National Institute for Petroleum and Energy Research	Dennis Brinkman John Goetzman

6. Pratt-Whitney Co.	Paul Warner Linda Neubauer
7. Dupont Co.	Tayman Phillips
8. EXXON R & E Co.	William Taylor
9. Texaco, Inc.	Salvatore Rand

APPENDIX H

DETAILED RESULTS OF COOPERATIVE TEST PROGRAM 3

TABLE H-I - RESULTS OF 65°C ACCELERATED TEST

LAB	Bottle No.	Peroxide Number, meq/kg Weeks Stressed at 65°C 0	1	2	3	4	6
		FUEL 1 - JET A (Texaco)					
NRL	A	.00	.15	.18	.26	.32	.44
	B	.00	.10	.18	.26	.74	.54
	C	.00	.12	.22	.27	.38	.51
	aver.	.00	.12	.20	.26	.48[b]	.50
NAPC	A	.00	.00	.41	.55	.76	1.94
	B	.00	.00	.51	.56	.64	2.03
	C	.00	.00	.44	.85	1.51	1.59
	aver.	.00	.00	.45	.65	.97[b]	1.85
P & W	A	.00	.04	.06	.10	.16	.15
	B	.00	.04	.07	.11	.14	.16
	C	.00	.02	.07	.11	.12	.16
	aver.	.00	.03[b]	.07	.11	.14	.16
duPont	A	.00	.03	.10		.16	.22
	B	.00	.04	.09		.09	.12
	C	.00	.04	.09		.12	.18
	aver.	.00	.04	.09		.12[b]	.17[b]
TEX	A	.00	.12	.49	.98	2.22	3.70
				.45		2.31	3.78
	B	--	.07	.34	.77	1.58	2.92
				.38		1.63	2.87
	aver.	.00	.10[b]	.42	.88	1.94	3.32
NIPER	1	.00	.07	.08	.08	.13	.12
	2	.00	.07	.08	.11	.13	.13
	3	.00	.10	.13	.15	.16	.15
	aver.	.00	.08	.09[b]	.11[b]	.14	.13
SwRI	1	.01	.30	.27	.55	.41	.43
	2	<.01	.43	.56	.14	.93	.47
	3	<.01	.20	.37	.52	.39	.42
	aver.	<.01	.31[b]	.40[b]	.40[a]	.58[b]	.44
EXXON	A	.00	.15	.15	.29	.28	.15
	B	.00	.13	.22	.34	.27	.18
	C	.00	.10	.18	.52	.32	.25
	aver.	.00	.13	.18	.38[b]	.29	.19[b]

[a] Ratio of highest to lowest bottle >3
[b] Ratio of highest to lowest bottle 1.5-3

TABLE H-I - Continued

LAB	Bottle No.	Peroxide Number, meq/kg — Weeks Stressed at 65°C: 0	1	2	3	4	6
		FUEL 2 - SHELL, MOD. PROC'D BLENDING STOCK					
NRL	A	.00	.00	.00	.00	.20	1.03
	B	.00	.00	.00	.05	.21	.76
	C	.00	.00	.00	.00	.16	.99
	aver.	.00	.00	.00	.02	.19	.93
NAPC	A	.00	.00	.00	.00	.49	4.99
	B	.00	.00	.00	.00	.00	1.20
	C	.00	.00	.00	.00	.00	1.64
	aver.	.00	.00	.00	.00	.16[a]	2.61[a]
P&W	A	.00	.00	.00	.00	.04	.14
	B	.00	.00	.00	.00	.05	.14
	C	.00	.00	.00	.00	.05	.15
	aver.	.00	.00	.00	.00	.05	.14
duPont	A	.00	.00	.00		.00	.24
	B	.00	.00	.00		.00	.29
	C	.00	.00	.00		.06	.32
	aver.	.00	.00	.00		.02[a]	.28
TEX	A	.00	.00	.00	.00	.10	.86
	B	-	.00	.00	.02	.14	.78
	aver.	.00	.00	.00	.01	.12	.82
NIPER	4	.00	.00	.00	.07	.27	.92
							.96
	5	.00	.00	.00	.18	.36	.95
							.96
	6	.00	.00	.19	.42	.74	1.45
	aver.	.00	.00	.06[a]	.22[a]	.46[b]	1.12[b]
SwRI	1	.03	<.01	<.01	.64	1.09	2.16
	2	<.01	<.01	<.01	<.01	.04	.70
	3	<.01	<.01	<.01	<.01	<.01	.63
	aver.	.01[a]	<.01	<.01	.21[a]	.38[a]	1.16[a]
EXXON	A	.00	.00	.01	.00	.00	.27
	B	.00	.00	.00	.00	.00	.14
	C	.00	.00	.00	.00	.00	.12
	aver.	.00	.00	.00	.00	.00	.18[b]

[a] Ratio of highest to lowest bottle >3

[b] Ratio of highest to lowest bottle 1.5-3

TABLE H-I - Continued

LAB	Bottle No.	Peroxide Number, meq/kg — Weeks Stressed at 65°C: 0	1	2	3	4	6
		FUEL 3 - SHELL, SEV. PROC'D. BLENDING STOCK					
NRL	A	.00	.00	.00	.00	.08	.21
	B	.00	.00	.00	.01	.07	.40
	C	.00	.00	.00	.06	.11	.48
	aver.	.00	.00	.00	.02[a]	.09	.36[b]
NAPC	A	.00	.00	.00	.00	.33	.01
	B	.00	.00	.00	.00	.18	.01
	C	.00	.00	.00	.17	1.21	1.97
	aver.	.00	.00	.00	.06[a]	.57[a]	.66[a]
P & W	A	.00	.00	.00	.05	.07	.12
	B	.00	.00	.00	.05	.08	.11
	C	--	.00	.00	.05	.08	.12
	aver.	.00	.00	.00	.05	.08	.12
duPont	A	.00	.00	.05		.07	.11
	B	.00	.00	.05		.07	.10
	C	.00	.00	.05		.08	.10
	aver.	.00	.00	.05		.07	.10
TEX	A	.00	.00	.03	.06	.09	.24
				.00			
	B	--	.00	.04	.06	.09	.27
	aver.	.00	.00	.03	.06	.09	.26
NIPER	7	.00	.00	.00	.00	.04	.11
							.11
	8	.00	.00	.00	.00	.00	.09
	9	.00	.04	.00	.00	.08	.22
	aver.	.00	.01	.00	.00	.04[a]	.14[b]
SwRI	1	.01	<.01	<.01	<.01	<.01	<.01
	2	<.01	<.01	<.01	<.01	<.01	<.01
	3	<.01	<.01	<.01	<.01	<.01	<.01
	aver.	<.01	<.01	<.01	<.01	<.01	<.01
EXXON	A	.00	.00	.00	.07	.05	.10
	B	.00	.00	.00	.00	.06	.07
	C	.00	.00	.00	.00	.04	.09
	aver.	.00	.00	.00	.02[a]	.05	.09

[a] Ratio of highest to lowest bottle >3
[b] Ratio of highest to lowest bottle 1.5-3

TABLE H-I - Continued

LAB	Bottle No.	Peroxide Number, meq/kg — Weeks Stressed at 65°C: 0	1	2	3	4	6
		FUEL 4 - PETRO-CANADA					
NRL	A	.00	1.56	31.4	103.0	207.5	361.2
	B	.00	7.32	64.5	158.0	257.0	460.8
	C	.00	2.89	37.2	156.2	236.4	345.0
	aver.	.00	3.92[a]	44.4[b]	139.1[b]	233.6	389.0
NAPC	A	.00	.00	25.1	67.4	94.6	297.8
	B	.00	.00	27.3	50.3	40.0	110.7
	C	.00	.00	24.6	142.2	288.9	317.5
	aver.	.00	.00	25.7	86.6[b]	141.1[a]	242.0[b]
P & W	A	.00	.14	11.9	96.1	237	471
	B	.00	.16	19.2	112.2	286	576
	C	--	.16	17.2	110.5	276	481
	aver.	.00	.15	16.1[b]	106.3	266	509
duPont	A	.00	.18	7.45		27.6	46.6
	B	.00	.18	9.50		38.4	56.5
	C	.00	.17	8.80		29.1	106.5
	aver.	.00	.18	8.58		31.7	69.9[b]
TEX	A	.00	5.48	58.1	174.8	237.3	374.3
			5.44	60.4	177.2	237.6	
				63.9			
	B	--	10.99	88.1	254.8	403.8	409.5
			11.74	76.3	260.1	409.4	
				87.1			
	aver.	.00	8.41[b]	72.5	216.7	322.0	391.9
NIPER	10	.00	.41	34.3	127.8	269.6	430.5
					129.8		427.2
	11	.00	.00	9.9	64.4	241.9	445.6
					66.4		443.6
	12	.00	.51	39.4	154.9	319.8	459.8
				43.9	167.9		
	aver.	.00	.31	28.6[a]	118.5[b]	277.1	444.4
SwRI	1	.02	.95	24.7	101.4	167.7	527.7
	2	<.01	.93	30.6	97.4	167.9	643.5
	3	<.01	.97	26.0	106.4	160.9	381.1
	aver.	.01	.95	27.1	101.7	165.5	517.4[b]
EXXON	A	.00	.00	8.70	38.1	65.0	83.0
	B	.00	.15	7.35	40.4	66.2	97.5
	C	.00	.03	4.38	31.8	64.5	75.3
	aver.	.00	.06[a]	6.81[b]	36.8	65.2	85.3

[a] Ratio of highest to lowest bottle >3
[b] Ratio of highest to lowest bottle 1.5-3

TABLE H-I - Continued

LAB	Bottle No.	Peroxide Number, meq/kg — Weeks Stressed at 65°C: 0	1	2	3	4	6
		FUEL 5 - SHALE JP-4					
NRL	A	.00	.06	.11	.91	8.01	42.1
					1.11		
	B	.00	.06	.08	.57	26.43	107.2
	C	.00	.08	4.65	25.95	63.79	110.7
	aver.	.00	.07	1.62[a]	9.18[a]	32.74[a]	86.7[b]
NAPC	A	.00	.00	.36	4.09	11.07	106.8
	B	.00	.00	.36	4.60	12.67	10.2
	C	.00	.00	.42	4.11	27.46	38.2
	aver.	.00	.00	.38	4.27	17.07[b]	51.7[a]
P & W	A	.00	.00	.12	2.6	20.4	97.1
	B	.00	.00	.12	2.3	19.1	110.6
	C	-	.00	.31	3.5	24.8	138.2
	aver.	.00	.00	.18[b]	2.8[b]	21.4	115.3
duPont	A	.00	.00	.07		2.07	52.4
	B	.00	.00	.06		1.89	44.2
	C	.00	.00	.07		1.78	52.8
	aver.	.00	.00	.07		1.91	49.8
TEX	A	.00	.08	4.54	28.3	75.4	257.5
				4.56	28.4	74.8	
	B	--	.18	8.18	35.4	90.9	278.8
				8.01	35.7	90.9	
	aver.	.00	.13[b]	6.30[b]	31.9	83.0	268.2
NIPER	13	.00	.00	.00	.03	.12	5.3
							5.5
	14	.00	.00	.00	.06	.33	33.9
							46.7
	15	.00	.00	.09	.72	13.9	105.8
						19.9	106.1
	aver.	.00	.00	.03[a]	.27[a]	5.78[a]	50.5[a]
SwRI	1	.06	<.01	.20	1.05	5.88*	60.0
	2	<.01	.04	.33	1.08	15.91	50.9
	3	<.01	.07	.29	.94	11.82	47.8
	aver.	.02[a]	.04[a]	.27[b]	1.02	13.87	52.9
EXXON	A	.00	.00	.15	17.2	48.9	67.5
					18.6	49.7	
	B	.00	.00	.13	4.41	19.9	
					4.60	18.7	48.8
	C	.00	.05	2.17	14.1	29.3	
					24.2	28.0	51.5
	aver.	.00	.02	.82[a]	12.2[a]	32.4[b]	55.9

[a] Ratio of highest to lowest bottle >3
[b] Ratio of highest to lowest bottle 1.5-3
* Sample size too large. Omit.

TABLE H-I - Continued

LAB	Bottle No.	Peroxide Number, meq/kg — Weeks Stressed at 65°C: 0	1	2	3	4	6
		FUEL 6 - JET A BLENDING STOCK, HYDROFINED					
NRL	A	.10	.53	1.58	2.71	5.55	70.7
	B	.10	.60	1.21	2.30	6.66	89.6
	C	.10	1.24	6.41	30.04	81.9	297.7
						74.0	
	aver.	.10	.79[b]	3.07[a]	11.7[a]	30.0[a]	152.7[a]
NAPC	A	.39	.00	2.69	5.13	5.14	66.5
	B	.38	.00	2.99	4.91	4.66	51.3
	C	.37	.00	2.65	4.90	10.18	38.2
	aver.	.38	.00	2.78	4.98	6.66[b]	52.0[b]
P & W	A	.08	.41	.90	1.9	3.8	22.2
	B	.09	.39	.91	1.9	4.2	19.0
	C	--	.39	.84	1.8	3.9	19.1
	aver	.09	.40	.88	1.9	4.0	20.1
duPont	A	.09	.70	1.80		7.75	23.8
	B	.09	.76	1.93		6.20	44.5
	C	.09	.66	1.78		6.75	22.1
	aver.	.09	.71	1.84		6.90	30.1[b]
TEX	A	.08	1.22	6.66	23.4	35.1	139.9
				6.62	23.7	35.7	135.8
	B	.09	.98	4.50	16.7	46.6	177.7
				4.56	16.7	46.7	183.2
	aver.	.09	1.10	5.59	20.1	41.0	159.2
NIPER	16	.09	.47	1.04	1.72	3.70	20.1
							21.6
	17	.09	1.44	3.03	16.08	63.6	225.3
					18.73	70.6	223.3
	18	.09	.68	2.11	5.99	18.1	196.3
					5.42	17.5	184.4
	aver.	.09	.86[a]	2.06[b]	8.3[a]	29.5[a]	145.2[a]
SwRI	1	.20	1.09	1.63	5.54	8.85	88.7
	2	.01	1.18	1.86	6.63	10.70	81.9
	3	.11	.94	2.02	6.17	11.33	110.1
	aver.	.14[a]	1.07	1.84	6.11	10.29	93.6
EXXON	A	.08	.52	1.11	1.83	3.01	16.3
	B	.07	.46	1.17	1.90	3.05	14.3
	C	.07	.49	1.17	1.77	2.73	11.7
	aver.	.07	.49	1.15	1.83	2.93	14.1

[a] Ratio of highest to lowest bottle >3

[b] Ratio of highest to lowest bottle 1.5-3

TABLE H-I - Continued

LAB	Bottle No.	Peroxide Number, meq/kg — Weeks Stressed at 65°C: 0	1	2	3	4	6
		FUEL 7 - JET A BLENDING STOCK, HYDROCRACKED					
NRL	A	.00	.13	.41	.35	2.68	102.3
	B	.00	.14	.62	1.63	3.51	122.2
	C	.00	.16	.43	1.15	3.64	79.7
	aver.	.00	.14	.49[b]	1.04[a]	3.28	101.4[b]
NAPC	A	.00	.00	.17	2.38	4.07	56.4
	B	.00	.00	1.08	3.01	3.77	34.9
	C	.00	.00	.54	1.78	5.31	12.8
	aver.	.00	.00	.60[a]	2.39[b]	4.38	34.7[a]
P & W	A	.00	.04	.21	1.10	4.2	39.9
	B	.00	.04	.15	.69	2.6	23.4
	C	--	.04	.20	.80	3.8	29.1
	aver.	.00	.04	.19	.86[b]	3.5[b]	30.8[b]
duPont	A	.00	.13	.35		2.75	26.9
	B	.00	.08	.37		4.12	29.3
	C	.00	.15	.35		3.70	27.0
	aver.	.00	.12[b]	.36		3.52	27.7
TEX	A	.00	.28	2.18	6.04	16.1	59.8
				2.07	6.07	15.7	59.3
	B	--	.25	2.70	8.61	24.2	156.2
				2.60	8.55	24.7	156.2
	aver.	.00	.27	2.39	7.32	20.2	107.9[b]
NIPER	19	.01	.06	.33	1.48	5.05	65.6
							65.2
	20	.01	.36	2.48	7.52	21.68	98.2
				2.94	8.51		96.8
	21	.00	.11	.63	5.67	23.25	161.0
					6.00		162.3
	aver.	.01	.17[a]	1.22[a]	5.11[a]	16.7[a]	108.2[b]
SwRI	1	.14	.77	1.12	4.65	6.63	63.3
	2	.02	.44	1.09	3.72	6.51	62.0
	3	<.01	.42	1.20	3.65	9.91	55.0
	aver.	.05[a]	.54[b]	1.14	4.01	7.68[b]	60.1
EXXON	A	.00	.00	2.33	6.94	16.6	50.8
				2.01		16.4	
	B	.00	.00	.96	6.23	17.2	50.1
				1.16		17.2	
	C	.00	.05	1.83	5.75	10.7	34.2
				1.61		11.0	
	aver.	.00	.02[a]	1.65[b]	6.31	14.9[a]	45.0

[a] Ratio of highest to lowest bottle >3
[b] Ratio of highest to lowest bottle 1.5-3

TABLE H-I - Continued

LAB	Bottle No.	Peroxide Number, meq/kg — Weeks Stressed at 65°C: 0	1	2	3	4	6
		FUEL 8 - JP-5 (EXXON, BATON ROUGE)					
NRL	A	.00	.05	.03	.06	.08	.08
	B	.02	.05	.03	.06	.10	.10
	C	.03	.04	.03	.04	.09	.09
	aver.	.02[a]	.05	.03	.05	.09	.09
NAPC	A	.00	.00	.16	.00	4.22[c]	.73
	B	.00	.00	.32	.00	.84	.77
	C	.00	.00	.17	.39	.95	1.12
	aver.	.00	.00	.22[b]	.13[a]	.90[a]	.87[b]
P & W	A	.00	.03	.06	.09	.07	.11
	B	.00	.02	.06	.09	.07	.11
	C	--	.04	.06	.09	.08	.11
	aver.	.00	.03[b]	.06	.09	.07	.11
duPont	A	.00	.00	.00		.03	.02
	B	.00	.00	.00		.00	.00
	C	.00	.00	.00		.00	.00
	aver.	.00	.00	.00		.01[a]	.01[a]
TEX	A	.01	.07	.14	.14	.17	.18
	B	.02	.05	.09	.13	.23	.20
	aver.	.02[b]	.06	.12[b]	.14	.20	.19
NIPER	22	.02	.05	.06	.06	.07	.08
	23	.02	.06	.08	.08	.11	.07
	24	.03	.05	.08	.06	.05	.07
	aver.	.02	.05	.07	.07	.08[b]	.07
SwRI	1	<.01	.20	.02	.11	<.01	.10
	2	<.01	.18	.17	.16	.12	.22
	3	<.01	.12	.12	.20	.41	.19
	aver.	<.01	.17[b]	.14[b]	.16[b]	.18[a]	.17[b]
EXXON	A	.00	.07	.08	.12	.06	.08
	B	.00	.04	.03	.10	.10	.07
	C	.01	.05	.09	.09	.07	.09
	aver.	.00	.05[b]	.07[a]	.11	.07[b]	.08

[a] Ratio of highest to lowest bottle >3
[b] Ratio of highest to lowest bottle 1.5-3
[c] Exclude this outlier.

TABLE H-I - Continued

LAB	Bottle No.	Peroxide Number, meq/kg — Weeks Stressed at 65°C: 0	1	2	3	4	6
		FUEL 9 - JP-5 (EXXON, BENICIA)					
NRL	A	.00	.00	.16	.39	.40	.79
	B	.00	.00	.19	.30	.37	1.75
	C	.00	.07	.24	.29	.43	.92
	aver.	.00	.02[a]	.20	.33	.40	1.15[b]
NAPC	A	.00	.00	.00	.51	1.05	8.72
	B	.00	.00	.00	.40	.53	9.61
	C	.00	.00	.39	.64	1.70	1.94
	aver.	.00	.00	.13[a]	.52[b]	1.09[a]	6.76[a]
P & W	A	.00	.00	.05	.16	.25	.46
	B	.00	.00	.04	.15	.29	.49
	C	--	.00	.04	.18	.26	.50
	aver.	.00	.00	.04	.16	.27	.48
duPont	A	.00	.00	.04		.33	.47
	B	.00	.00	.04		.30	.49
	C	.00	.00	.04		.24	.53
	aver.	.00	.00	.04		.29	.50
TEX	A	.00	.01	.12	.21	.30	.55
							.56
	B	--	.02	.13	.22	.44	.92
							.94
	aver.	.00	.02[b]	.13	.22	.37	.74[b]
NIPER	25	.00	.00	.09	.14	.18	.43
	26	.00	.00	.18	.35	.49	.76
	27	.00	.00	.09	.20	.30	.49
	aver.	.00	.00	.12[b]	.23[b]	.32[b]	.56[b]
SwRI	A	.18	.20	.47	.85	.88	1.32
	B	<.01	.32	.58	1.02	1.02	1.03
	C	.03	.03	.53	.29	.53	.77
	aver.	.07[a]	.18[a]	.53	.72[a]	.81[b]	1.04[b]
EXXON	A	.00	.00	.17	.34	.39	.55
	B	.00	.00	.10	.23	.30	.52
	C	.00	.00	.11	.16	.28	.58
	aver.	.00	.00	.13[b]	.24[b]	.32	.55

[a] Ratio of highest to lowest bottle >3
[b] Ratio of highest to lowest bottle 1.5-3

TABLE H-II - VARIABILITY OF TRIPLICATE FUEL SAMPLES

	Percent Difference Between Triplicates*					
	Weeks Stressed at 65°C					
LAB	0	1	2	3	4	6
			FUEL 1			
NRL	0	41	21	4	88	20
NAPC	0	0	22	46	77	24
P & W	0	61	15	9	29	6
duPont	0	27	11		57	58
TEX		53	27	24	35	15
NIPER	0	38	52	52	21	24
SwRI	0	74	73	103	93	11
EXXON	0	39	38	61	17	53
			FUEL 2			
NRL	0	0	0		26	29
NAPC	0	0	0	0	301	145
P & W	0	0	0	0	21	7
duPont	0	0	0			29
TEX		0	0		33	10
NIPER	0	0	302	159	104	46
SwRI		0	0	300	186	132
EXXON	0	0	0	0	0	83
			FUEL 3			
NRL	0	0	0	261	44	75
NAPC	0	0	0	300	181	296
P & W	0	0	0	0	13	9
duPont	0	0	0		13	10
TEX		0	29	0	0	12
NIPER	0		0	0		93
SwRI	0	0	0	0	0	0
EXXON	0	0	0		40	33

* $\frac{\text{range}}{\text{mean}} \times 100$

Note: A range of 1.5:1 = 40% difference.
A range of 3:1 = 100% difference.

TABLE H-II - Continued

LAB	Percent Difference Between Triplicates* Weeks Stressed at 65°C 0	1	2	3	4	6
			FUEL 4			
NRL	0	147	75	40	22	30
NAPC	0	0	11	106	176	90
P & W	0	13	45	15	18	21
duPont	0	6	24		34	36
TEX	0	64	32	38	52	9
NIPER	0		111	81	28	7
SwRI	0	4	22	9	4	51
EXXON	0		63	23	3	26
			FUEL 5			
NRL	0	37	280	276	171	68
NAPC	0	0	16	12	10	187
P & W	0	0	100	43	27	36
duPont	0	0	15		15	17
TEX	0	77	57	23	19	8
NIPER	0	0		256	291	199
SwRI			48	14	30	23
EXXON	0		249	110	93	33
			FUEL 6			
NRL	0	90	202	233	241	262
NAPC	5	0	12	5	82	54
P & W	12	5	10	5	10	16
duPont	0	14	8		22	74
TEX	12	22	38	34	28	28
NIPER	0	113	97	189	215	140
SwRI	173	22	21	18	24	30
EXXON	14	121	5	7	11	33

$* \ \frac{\text{range}}{\text{mean}} \times 100$

Note: A range of 1.5:1 = 40% difference.
A range of 3:1 = 100% difference.

TABLE H-II - Continued

LAB	Percent Difference Between Triplicates* — Weeks Stressed at 65°C: 0	1	2	3	4	5
FUEL 7						
NRL	0	21	43	123	29	42
NAPC	0	0	152	51	35	126
P & W	0	0	32	48	45	54
duPont	0	58	6		39	9
TEX	0	11	22	34	43	90
NIPER	0	167	195	127	109	89
SwRI	280	65	10	25	44	14
EXXON	0	300	64	19	42	37
FUEL 8						
NRL		31	22	40	20	20
NAPC	0	0	74	300	169	45
P & W	0	67	0	0	13	0
duPont	0	0	0			
TEX		33	43	7	30	11
NIPER		25	18	40	50	17
SwRI	0	47	107	57	228	71
EXXON	0	60	86	27	57	25
FUEL 9						
NRL	0		39	30	15	83
NAPC	0	0	300	46	107	113
P & W	0	0	23	18	15	8
duPont	0	0	0		31	12
TEX	0	67	8	5	38	49
NIPER	0	0	82	92	92	59
SwRI	245	161	21	115	60	53
EXXON	0	0	54	75	34	11

* $\frac{\text{range}}{\text{mean}} \times 100$

Note: A range of 1.5:1 = 40% difference.
A range of 3:1 = 100% difference.

TABLE H-III - CONTROL SAMPLE RESULTS

(Peroxide Number, meq/kg)

1. NRL

3 Weeks		5 Weeks		
25 ml	10 ml	25 ml	10 ml	50 ml
2.350	2.633	2.254	2.489	2.060
2.339	2.519	2.248	2.690	
2.315		2.314		
2.431		2.233		
2.364		2.246		
2.360*	2.576	2.259	2.590	2.060
4.9%*	4.4%	3.6%	7.8%	

2. NAPC

2 Weeks	6 Weeks	9 Weeks
3.72	2.94	1.90
3.52	3.03	2.10
3.78		1.91
3.67	2.99	1.97
7.1%	3.0%	9.6%

3. P&W

1 Week	3 Weeks
2.02	2.05
2.03	2.01
2.13	2.02
2.02	2.05
2.05	2.03
5.4%	2.0%

4. duPont

6 Weeks
1.84
1.89
1.87
2.7%

5. Texaco

2 Weeks	4 Weeks
2.13	2.17
2.09	2.21
2.16	2.03
2.10	2.23
2.12	2.16
3.3%	9.3%

TABLE H-III - Continued

6. NIPER

2 Weeks	4 Weeks
2.310	2.331
2.425	2.287
2.334	2.353
2.473	2.324
	2.264
2.386	2.312
6.8%	3.8%

7. SwRI

2 Weeks	4 Weeks
2.25	2.30
2.54	2.23
2.50	2.60
2.63	2.22
2.48	2.34
15.3%	16.2%

8. EXXON

Initial (8/27/86)	2 Weeks
1.6783	1.5107
1.5844	1.2807
1.6635	1.3701
1.7252	1.5181
1.6629	1.4199
8.5%	17.0%

* The first value is the average and the second is the ratio of the range to the average as a percent.

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