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STORAGE STABILITY OF GASOLINE

DEVELOPMENT OF A STABILITY PREDICTION METHOD AND STUDIES OF GASOLINE COMPOSITION AND COMPONENT REACTIVITY

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DEVELOPMENT OF A STABILITY PREDICTION METHOD AND STUDIES OF GASOLINE COMPOSITION AND COMPONENT REACTIVITY

by

F. G. Schwartz,[1] M. L. Whisman,[2] C. S. Allbright,[3] and C. C. Ward [4]

ABSTRACT

The Bureau of Mines developed a rapid and precise method for predicting storage stability of motor gasolines. This method resulted from the investigation of many analytical techniques as well as a study of fuel composition and fuel component gum-forming mechanisms. The first section of this bulletin discusses the development of the prediction test through its several phases, including revision of the standard 110° F storage test; attempts to develop a modification of the ASTM D525 induction bomb test; and the ultimate abandonment of this procedure with the adoption of the 16-hour oven test that was both precise and rapid. The second section comprises a discussion of further studies of fuel composition, including the reactivity of certain sulfur compounds and hydrocarbons to form gum. The compositions of various gums and inorganic deposits are reported in terms of elemental analysis and spectroscopic examinations. The reactions of tetraethyllead with selected hydrocarbons are also reported.

INTRODUCTION

Gasoline is a complex mixture of hydrocarbons and organic compounds containing sulfur and nitrogen. When gasoline is stored for extended intervals before use, some of these compounds react with oxygen in the air and with one another to form new, higher-molecular-weight materials commonly called gum. The ability of a gasoline to resist such changes in its composition as time passes is referred to as its stability. Insufficient stability of gasoline during prolonged storage is a problem that first became notably serious about 1920 when the increased demand for gasoline led to greater use of thermal cracking. These thermally cracked products oxidize more readily than does straight-run material, resulting in the quick development of gum. Upon evaporation of the gasoline, these gums appear as a hard or sticky residue, and they may deposit in the induction system of an engine and cause malfunction. Tetraethyllead and other lead alkyls are also subject to oxidation, with the consequent formation of haze or precipitates that cause physical plugging of filters, fouling of valves, and blocking of orifices.

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Most gasolines used by the general public are moved from the refinery to the consumer's gas tank quickly enough to avoid problems associated with storage stability. However, the Department of Defense, whose supplies and stores of gasolines literally encircle the earth, faces a different situation. These stores must remain suitable for use for several years, and many modern gasolines will not meet this requirement. What is needed, then, is a rapid and precise test method for predicting whether or not a fuel will resist oxidation and the resulting degradation. The standard test is an ASTM method designated as D525 (*8*),[5] often called the induction period test. The test, however, is generally regarded as being unreliable for predicting the storage stability characteristics of gasolines (*1–8, 10–11, 12–14, 20*).

Because of the Bureau's extensive experience in refining processes as well as the utilization of petroleum products, a cooperative research program under the sponsorship of the Research Division, Army Materiel Command, was started in 1954. The project was established because of the inadequacy of existing methods for accelerated aging to predict storage stability of motor gasolines. The objective of the research was to accumulate fundamental information relating to fuel stability that would serve as the basis for developing a procedure for predicting the storage stability of fuels.

The Bureau's contribution to these investigations through June 1963 was reported in a series of publications (*23, 28–36, 43–45*) and a summary bulletin (*37*). These accomplishments included a study of the variables of composition and environment affecting storage stability of gasoline-type fuels. Radiotracers and other analytical techniques were utilized in the study. Changes in fuel composition brought about by aging were determined and correlated with gum formation. It was shown that sulfur and nitrogen compounds in combination with aromatics and olefin enter into gum-forming processes.

ACKNOWLEDGMENTS

This research was made possible through the sponsorship of the Research Division, Army Materiel Command, and its funds were used to finance part of the program. The advice of Research Division personnel was of great value throughout the program. The helpful guidance of the Advisory Group on Fundamentals of Storage Stability of the Coordinating Research Council (CRC) also is gratefully acknowledged. The contributions and analyses provided by Jack H. Hale, R. F. Kendall, J. E. Dooley, and Otha Davis, all Bureau of Mines personnel, were valuable additions to this effort and are hereby gratefully acknowledged.

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

MOTOR GASOLINE STORAGE STABILITY

Standard methods (*7*) were sufficient to accurately measure the existent gum of gasolines and resistance to further oxidation, but reliable accelerated test procedures for predicting storage stability were not available at the outset of this program. Standard storage-stability evaluation procedures included either ambient temperature storage or a mildly accelerated test accomplished by storing at 110° F. Few investigators were willing to accept more severe conditions of thermal stress than these; evaluation of storage stability was therefore a long-term process. At least 16 weeks' storage at 110° F, corresponding roughly to 3 years of ambient (80° F) storage, were required to get a reliable measure of fuel stability (*42*). In the development of a more rapid and yet precise method of predicting storage stability, the studies were divided into four phases: First, it was necessary to revise the standard 110° F storage procedures to ensure an adequate supply of oxygen to samples. The second and third phases were pointed toward modification of ASTM D525 induction bomb tests (*8*) for storage stability to improve the correlation between these results and those obtained in 110° F storage. The final phase was abandonment of the induction period bomb and the development of a 16-hour oven test (*24*) that met requirements of precision, accuracy, and time, and also achieved the required correlation with 110° F storage. Details of these investigations are described in that order in this bulletin.

110° F STORAGE TEST

The storage procedure used to evaluate fuel stability until 1965 has been described (*37*). Briefly, it was an adaptation of a generally accepted method and involved storing replicate samples in 22-oz bottles which were capped and sealed tightly. These were placed in a hot room thermostated at 110° F, and one bottle was removed for analysis at each desired storage period. The air-fuel ratio in these bottles was about 0.86

Table 1.—*Comparison of gum formation of fuels in sealed storage, and fuels with air replenishment*

Sample	Storage period at 110° F									
	0 weeks		3 weeks		8 weeks		16 weeks		32 weeks	
	Gum, mg/100 ml	O_2, pct	Gum, mg/100 ml	O_2, pct	Gum, mg/100 ml	O_2, pct	Gum, mg/100 ml	O_2, pct	Gum, mg/100 ml	O_2, pct
BOG–185:										
Sealed [1]	1.9	21	3.2	20	5.4	14	11.1	4	15.9	0
Air replenished [2]	1.9	21	4.1	20	6.4	19	13.7	19	37.8	13
BOG–186:										
Sealed [1]	1.1	21	2.8	20	2.0	20	2.5	18	2.3	17
Air replenished [2]	1.1	21	2.2	21	1.3	20	2.4	20	5.9	20
BOG–193:										
Sealed [1]	1.8	21	2.0	20	4.4	19	6.5	13	9.2	15
Air replenished [2]	1.8	--	2.1	20	6.3	21	6.3	19	25.7	15
BOG–194:										
Sealed [1]	0	21	.6	21	0	21	0	21	0	7
Air replenished [2]	0	--	0	21	.3	21	.2	20	.8	20
BOG–195:										
Sealed [1]	1.6	21	3.2	21	3.9	21	3.9	10	5.0	9
Air replenished [2]	1.6	--	3.3	21	1.3	21	3.1	20	7.7	17
BOG–196:										
Sealed [1]	3.5	21	9.1	16	13.1	1	13.9	1	13.1	0
Air replenished [2]	3.5	--	40.2	10	54.3	10	123.8	0	401.0	0
BOG–202:										
Sealed [1]	1.4	21	2.5	18	4.0	16	8.5	0	9.3	0
Air replenished [2]	1.4	21	6.5	19	6.5	17	16.7	14	105.8	7
BOG–295:										
Sealed [1]	0	21	.6	21	0	21	0	21	0	7
Air replenished [2]	0	21	.6	21	--	--	1.6	20	1.9	20

[1] Averages of two tests.
[2] Averages of duplicate determination of each of two bottles.

(350 ml of fuel in a 650-ml bottle). It was observed, however, that some samples ran out of oxygen before reaching the end of the desired storage period. This obviously limited gum formation resulting from oxidation processes. Therefore, in 1966, the storage test procedure was modified to include the use of a larger 40-oz bottle with an air-fuel ratio of 2.38. The bottles were sealed as before, but they were opened and the air was replenished every 4 weeks through-

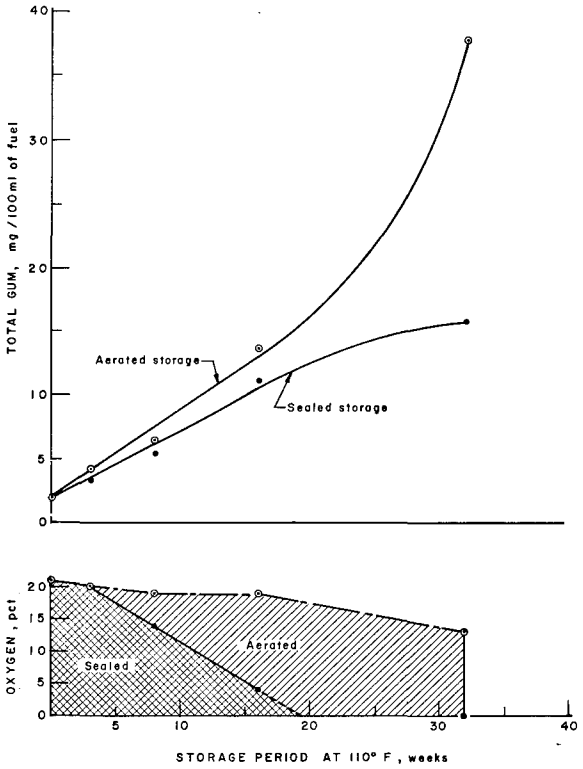


Figure 1.—Comparison of gum and oxygen levels during sealed and aerated storage of BOG–185.

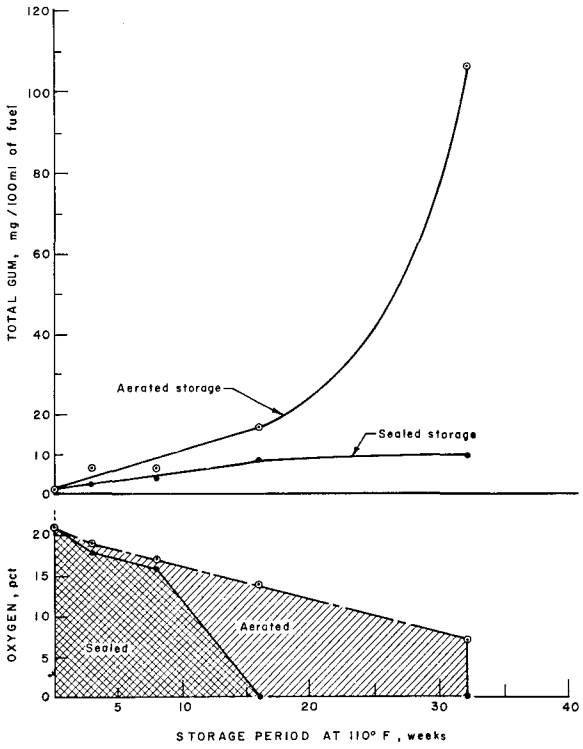


Figure 3.—Comparison of gum and oxygen levels during sealed and aerated storage of BOG–202.

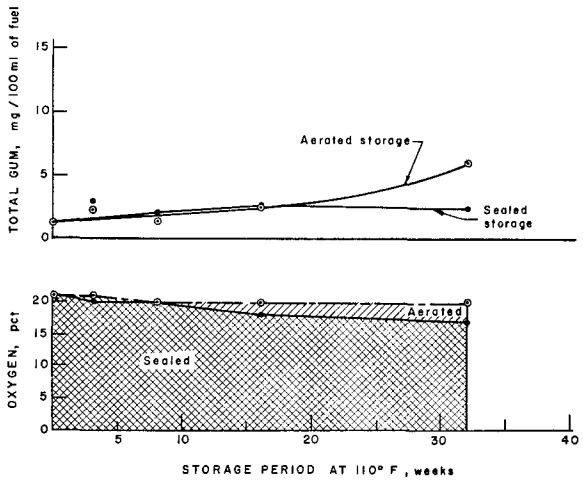


Figure 2.—Comparison of gum and oxygen levels during sealed and aerated storage of BOG–186.

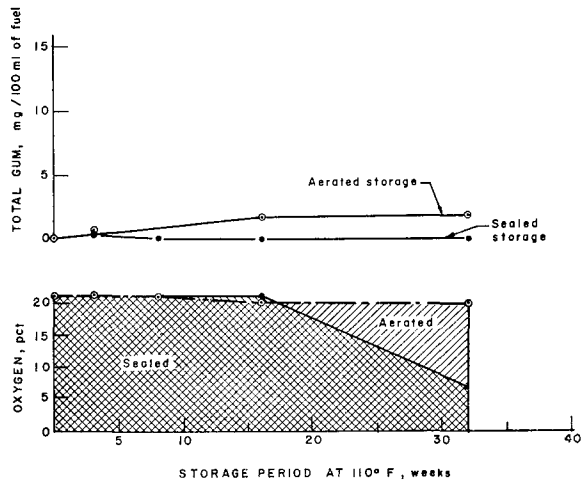


Figure 4.—Comparison of gum and oxygen levels during sealed and aerated storage of BOG–295.

out the entire storage period. To further facilitate the monitoring of oxygen consumption, these bottles were equipped with a septum-type closure, so that the sample outage could be analyzed without opening the container. Details of this test are included in section A1 of appendix A. The volume of oxygen in the space over the sample was determined by piercing the septum with a hypodermic syringe and removing an aliquot. Oxygen was determined by a gas chromatographic method described in appendix A (section A3). The other measure of deterioration used on these samples was the determination of total gum, which was the sum of insoluble and soluble gums. These methods are also described in appendix A, section A2. The effect of altering the storage containers and procedures can be observed from data in table I. It is obvious at the 32-week period that oxygen replenishment dramatically increased the quantity of gum formed in all fuels.

The dependence of gum-forming rate upon available oxygen is more clearly evident from graphs of the data in figures 1–4. The time-gum curves appear in the upper part of the figure; the amounts of oxygen found in the air of the vapor space at corresponding storage intervals are shown in the lower part of each figure. These curves indicate that gum formation generally levels off after oxygen depletion. Stable fuels showed little or no significant differences between sealed and aerated storage, but obviously the gum-forming mechanism is primarily an oxidation process and limiting the supply of oxygen during testing can often give misleading results.

OTHER ACCELERATED TESTS

ASTM D525

The most generally used method for predicting gasoline storage stability is the so-called induction period bomb test. The significance of test results from this method has been questioned (*6, 10–11, 13–14, 20*), and today the test is considered unreliable for predicting the behavior of fuels under ambient or mildly accelerated (110° F) conditions of storage. A major part of this research was directed toward the ultimate development of a rapid and precise prediction method of motor gasoline storage stability. First efforts were pointed toward a modification of the D525 induction period bomb test.

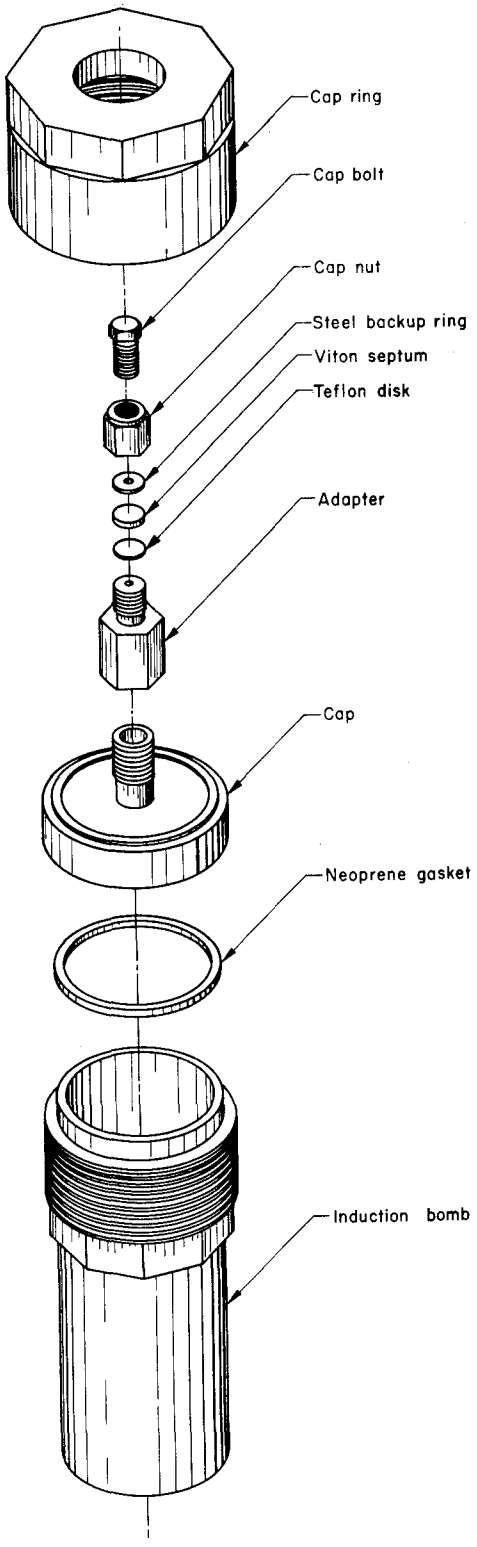


Figure 5.—Modified induction period bomb used in rapid test for stability.

Development of a Modified Induction Bomb Test

These modifications included both equipment and procedure. The ASTM D525 metal bomb was used, but it was converted to a sealed system and provision was made for sampling the bomb atmosphere before opening the container at the end of the test period. Figure 5 shows the metal container as modified for this study. The glass liner used in the standard test procedure was omitted.

For initial tests, 100-ml samples were used. The sample was first placed in the bomb. The bomb was then sealed, using a new gasket for each test, and heated to the specified temperature for the specified time in an oven. Both temperature and time were varied in initial tests in searching for the best test conditions. Times of 4, 8, and 16 hours were used, as well as temperatures of 300°, 250°, 200°, and 150° F. Other changes in procedure included cleaning procedures and replicated gum determination. At the end of the test period, the bombs were removed from the oven and quenched in cold water. The oxygen in the outage was determined, the bombs were opened, and percent light transmission, air-jet gum, and gas chromatographic analyses were made on the stressed fuel. The amounts of gum formed in preliminary tests in the bombs are listed in table 2. Inspection of these data led to the decision that a temperature of 150° F was not high enough to produce the acceleration desired. At the other extreme, 300° F appeared to yield erratic results. Between these extremes was a temperature more satisfactory for our purposes.

Arbitrarily, 250° F was selected as the compromise temperature for subsequent testing, and a set of standard test conditions was established:

1. Before each test, the bombs were cleaned by an electrolytic cleaning process (*45*) to assure a reproducible, clean surface.
2. Each fuel was oven-aged for 4, 8, and 16 hours at 250° F.
3. Four bombs were used to test each fuel at each condition of testing. After aging, the contents of the bombs were mixed to provide a composite sample for analyses in which bomb difference was not a variable.
4. To minimize errors in air-jet gum determination, six determinations were made on the combined filtered sample and the results were averaged to obtain the air-jet gum level.
5. Total gum, fuel insoluble gum plus air-jet gum, was determined as a basis for correlation.

Test Results

Results obtained from these test conditions indicated that there was an inadequate supply of oxygen in the bomb during the longer periods of testing. For this reason, further modification of the test was required to ensure adequate oxygen in the bomb for the duration of the test. At a test temperature of 250° F, even small samples consumed the entire oxygen content of the outage during a 16-hour test. Table 3 shows some of the data obtained that show the inadequacy of oxygen for the entire test period. Subsequently, further modifications to the test procedure were adopted, including a test temperature of 200° F with a sample volume of 55 ml. This proved to be an improvement, as shown by data in table 3. A further modification was the analysis of individual bomb samples rather than a composite.

Correlations Between the Modified Induction Bomb Test and Standard Storage

Original correlations derived with data from the modified induction bomb test were quite promising. However, extended use of the equipment and repeated cleaning of the bombs produced deviations outside the statistical limits obtained from initial data. It was apparent after these deviations developed that a further modification involving the fuel container was necessary. However, the promising correlations obtained indicated the practicality of the general

Table 2.—*Gum formation in modified induction period bomb* [1]

	Gum, mg/100 ml											
	16-hr test				8-hr test				4-hr test			
Temperature, ° F	300°	250°	200°	150°	300°	250°	200°	150°	300°	250°	200°	150°
BOG–185	45.2	43.3	12.6	3.0	17.3	19.5	4.2	--	10.5	6.3	--	--
BOG–193	32.8	23.0	13.7	6.5	20.3	23.7	3.6	--	17.1	6.1	--	--
BOG–195	37.8	21.6	9.9	5.0	27.4	10.0	2.5	--	11.0	3.5	--	--
BOG–196	28.8	21.9	20.7	7.3	24.9	26.6	16.2	--	17.3	14.9	--	--
BOG–202	56.7	36.9	11.6	5.7	33.7	11.7	1.4	--	12.1	5.8	--	--

[1] Sum of insoluble and air-jet gum; average of 2 bombs.

Table 3.—*Effect of temperature and air-fuel ratio on gum formation*

Sample	Time in bomb, hr							
	0		4		8		16	
	Gum, mg/100 ml fuel	O_2, pct	Gum, mg/100 ml fuel	O_2, pct	Gum, mg/100 ml fuel	O_2, pct	Gum, mg/100 ml fuel	O_2, pct
				1:1 AIR-FUEL RATIO, 250° F				
BOG–185	1.9	--	6.2	8	11.6	0	15.5	1
BOG–186	1.1	--	2.7	18	7.0	4	9.2	0
BOG–193	1.8	--	6.3	5	11.1	0	13.0	0
BOG–194	0	--	0	20	0	16	.2	8
BOG–195	1.6	--	5.7	17	8.9	5	12.7	2
BOG–202	1.4	--	6.5	5	8.9	0	12.9	0
				3:1 AIR-FUEL RATIO, 200° F				
BOG–185	1.9	--	--	--	7.2	19	13.3	11
BOG–186	1.1	--	--	--	4.3	19	4.2	18
BOG–193	1.8	--	--	--	4.4	19	11.3	11.5
BOG–194	0	--	--	--	1.5	20	1.5	20
BOG–195	1.6	--	--	--	3.5	21	10.7	20
BOG–202	1.4	--	--	--	3.5	21	12.1	7
BOG–295	0	--	--	--	4.3	21	1.1	21

approach, and the statistical treatment of these initial data are therefore included.

Data in table C–1 show the results of applying the modified induction period bomb test to four fuels, both neat and containing additives. Table C–2 shows the test data for the same samples obtained by storing at 110° F for up to 32 weeks. Examination of the data showing total gum formed in fuels during storage and in the bomb showed that in most instances the gum which formed under the two conditions was comparable, but not consistent enough to use gum formation in the bomb test as a prediction method. It also was noted that in those instances where the bomb results were low, the oxygen remaining in the bomb was low, indicating that gum formation had been retarded by oxygen depletion. Therefore, the data were studied to determine if a better correlation could be obtained by adjusting the value for the amount of gum formed in the bomb by taking into account the amount of oxygen consumed. The best correlation developed was a prediction curve that used an *F* factor, which was obtained by dividing the amount of total gum formed after the bomb test by the percent oxygen in the bomb after the test. In those cases where the oxygen was exhausted, an arbitrary value of 1 percent oxygen was used to avoid dividing by zero.

The *F* values for the fuels without additives were plotted against the total gum from storage to develop the curves shown in figure C–1. Similar curves are shown for leaded fuels in figure C–2. Direct plots of inorganic residue in the bomb (16 hours) and in storage (16- and 32-week periods) are shown in figure C–3. These three figures were used to estimate from bomb data the total gum formation in 110° F storage in nonadditive fuels, in leaded fuels, in fuels containing antioxidants only, and inorganic residue precipitated from leaded fuels.

The results of stability prediction for neat fuels using the curves in figure C–1 are listed in table C–3. An examination of these data shows that a reasonable prediction of total gum formation was made in 25 cases out of a possible 28. That is, the predicted value was acceptable 89 percent of the time.

Eight of the blends studied in the program were neat fuels with an added antioxidant. Although test results from these samples were not used in developing the correlations, the data showed that the neat fuel prediction curves fitted the antioxidant blends, so *F* values based on the 16-hour test were calculated, and predicted gum values obtained through figure C–1. Determined and predicted values are given in table C–4 for the fuels with antioxidants. In these blends, an acceptable prediction of total gum formation was made in 27 cases out of a possible 32, or an acceptable prediction 84 percent of the time.

Predictions of total gum formation in leaded blends are shown in the data listed in table C–5. Forty-eight predictions were made, and the predicted value was acceptable (considering gum level as well as deviation) in 36 of the predictions, or 75 percent of the time.

Significant quantities of inorganic precipitate were recovered from the leaded fuels after 16

hours and 16 weeks of stability testing. Figure C–3 permits estimations of the fuel-insoluble inorganic residue that will form during storage for 16- and 32-week periods, from 16-hour bomb data. The determined values of inorganic residue and corresponding predicted values are shown in table C–6. In this table, insoluble residue (lead precipitate) formation was predicted for 48 tests. In only eight of these tests was the predicted value unacceptable. This represented an 83-percent acceptability.

All of the gum formation predictions presented are on a total gum (insoluble gum + soluble gum) basis. The soluble gum usually constitutes 90 percent of the total gum. Using total gum permits a good estimate of the split between the two types of gum. This is achieved by taking 10 percent of the total gum as the amount of insoluble gum; the remainder will be soluble gum. This is an excellent relationship, with only three or four points off of the line. For instance, figure C–4 shows the results of plotting total gum against soluble gum for all of the samples stored at 110° F. Thus, using figure C–4 and a total gum figure, estimates of the amounts of insoluble and soluble gum can be made. Complete details of this study have been reported (*3*).

Development of a 16-Hour Oven Test for Motor Gasoline Storage Stability Prediction

Difficulties that arose with the modified ASTM Induction Period Bomb Test in the form of erratic results were eventually attributed to the interior surface condition of the bomb itself. It was postulated that electropolishing the bomb interior after each test—although effective for cleaning—altered the surface porosity or area such that results soon became unacceptably erratic. Therefore, an entirely new concept in storage containers was sought. Glass bottles were attractive from the standpoint of inertness, ease of cleaning, and simplicity of closure systems, but were considered something of a hazard for storing flammable material at elevated temperatures. These objections were eventually met satisfactorily, and the test procedure was modified to include the use of 16-oz bottles equivalent to Owens-Illinois Mold No. G–20141 [6] glass (*23–25*). Twenty-four gasolines were tested by the technique that was developed, and correlations were established with results from 110° F storage. Development of the final test method, which is detailed in section C of appendix A, resulted from these studies and from the expertise and experience acquired by the research staff at the Bureau's Bartlesville Energy Research Center in the investigation of all aspects of storage stability of fuels during the past two decades (*2–4, 23–25, 28–36, 43–54*).

[6] Reference to specific trade names is made for identification only and does not imply endorsement by the Bureau of Mines.

Procedure

The oven tests (see section B, appendix A) were made for 16 hours at 200° F with 130 ml of gasoline in 16-oz, pressure-type beverage bottles. The bottles were capped with a special cap to permit sampling of the outage in the bottle for determination of oxygen content. The bottle and cap are diagramed in figure A–2. The bottles were encased in cylindrical safety shields (fig. A–3) for protection of personnel in case of breakage.

Fuel deterioration in both storage and oven tests was measured by determination of inorganic residue, insoluble gum, and soluble gum, all in milligrams per 100 ml of fuel; in addition, for the oven-test samples, percent oxygen in air in bottle outage at end of test was also determined.

To determine these properties, the aged sample was filtered and soluble (air-jet) gum was determined on the filtrate by ASTM Method D381 (*7*). Insoluble gum was removed from the inorganic residue by washing the filter with a solvent that consisted of equal parts of benzene, methanol, and acetone. The solvent was allowed to evaporate from the filtrate, and the residue was weighed to measure the insoluble gum. The inorganic residue was obtained by differential weighing of the filter. The filtering apparatus was assembled as shown in figure A–1.

The outage of the bottle used in the oven-test procedure was sampled (see section A3, appendix A) through the septum by using a chromatographic, microliter hypodermic syringe. The withdrawn sample was charged to a gas chromatograph to obtain a gas analysis. This yielded an oxygen-argon peak and a nitrogen peak. Oxygen content was calculated from the ratio of the nitrogen and oxygen peak heights, corrected for argon, and compared with peaks from air as a reference standard.

Data were obtained on 24 gasolines for evaluation of this test method. These fuels, described in detail in tables B–1 and B–2, included 13 commercial- and military-specification gasolines (fuels 1 through 13) and 11 fuels that were specially blended (fuels 14–24) to give a wide range in hydrocarbon-type composition. All fuels were leaded and inhibited. Table B–1 shows the available information concerning composition

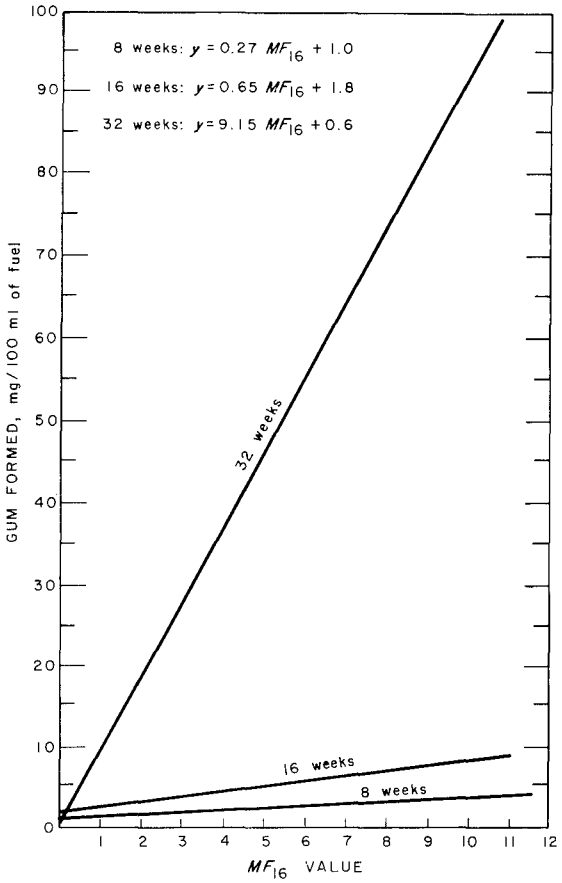


Figure 6.—Relationship of gum formed during storage to MF_{16} value.

and additives in the latter 11 fuels. The results of these tests by both the 16-hour oven test and standard 110° F storage are shown in table C–7.

Correlation of 16-Hour Oven Test Data With 110° F Storage Data

The data obtained on the 24 gasolines before storage, after various periods of 110° F storage, and from the 16-hour oven test were used in deriving a set of general equations that describe the storage stability characteristics of each fuel. The equation relates the amount of oxygen that reacted during the 16-hour oven test and the total gum that formed during the same period with the stability characteristics as described by the standard 110° F test. The final equation that was developed is shown below:

$$G_{110} = m\ (MF_{16}) + G_0 + C, \quad (1)$$

where G_{110} = predicted value for total gum during 110° F storage, mg/100 ml,
m = slope of the "gum-MF_{16}" line for each 110° F storage period,
MF_{16} = multiplying factor calculated from 16-hour test for each gasoline,
G_0 = initial gum, mg/100 ml,
and C = constant equal to average intercept for gum lines.

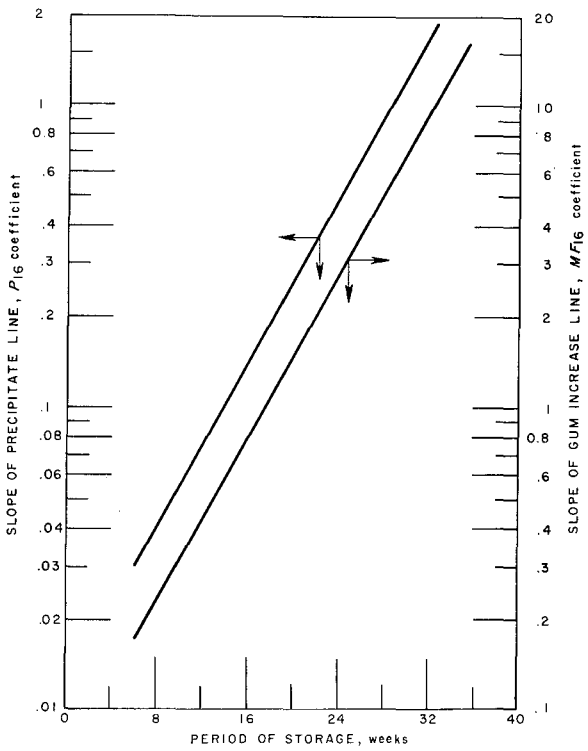


Figure 7.—Slopes of gum and precipitate lines related to storage period.

The values for the terms in equation 1 were obtained as follows:

$$MF_{16} = \frac{\text{pct } O_0 - \text{pct } O_{16}}{\text{pct } O_0}\,(G_{16} - G_0), \quad (2)$$

where pct O_0 = 21, percent oxygen in air,
pct O_{16} = percent oxygen in air in outage at end of oven test,
G_{16} = gum content, soluble plus insoluble, at end of oven test, mg/100 ml,
and G_0 = gum content, soluble plus insoluble, in fresh fuel, mg/100 ml.

The value of m, the slope of the gum-MF_{16} line, was determined by plotting the MF_{16} value for each of the 24 gasolines against the increase in total gum that occurred during 8 weeks of storage. The equation of the line of best fit to the points was then developed by statistical analysis. Figure 6 presents the plot for the 8-week storage data. The line, which is a least-squares fit to the data, has a slope (m) of 0.27 and an intercept value of 1.0. Similarly, slopes for the 16- and 32-week lines were 0.65 and 9.15, and intercepts were 1.8 and 0.6, respectively. Figure

6 also presents these lines and equations. Although the 52-week data correlated rather poorly, it was concluded that 32 weeks of storage at 110° F was adequate, because that is equivalent to storage for more than 5 years, as shown later in this report.

In figure 7, the slope values are plotted on a logarithmic scale against storage period in weeks on a linear scale. Use of this figure enables one to estimate the slope, m, for any storage time in the interval 8 to 32 weeks. Substitution of an average intercept value of 1.2 and slopes taken from figure 7 into the general equation gave the following equations for predicting the gum at the stated intervals of storage, in mg/100 ml:

8 weeks at 110° F: Total gum $= 0.23\ MF_{16} + G_0 + 1.2$
16 weeks at 110° F: Total gum $= 0.78\ MF_{16} + G_0 + 1.2$
32 weeks at 110° F: Total gum $= 9.15\ MF_{16} + G_0 + 1.2$

The amounts of gum that would form in each of the 24 gasolines during these periods of storage were predicted by solving the equations. In figure 8 the results are compared graphically with values determined during storage. Gum values above 10 seldom exist in commercial gasolines, so gum values below 10 are shown on an expanded scale in the inset for the figure.

Data obtained on the gasolines before storage, after 110° F storage, and from the 16-hour oven test were used to develop general equation 3 that relates the amount of lead precipitate formed in the oven test to the amount formed during storage:

$$P_{110} = m\ (P_{16}) + C, \qquad (3)$$

where P_{110} = predicted value for precipitate during 110° F storage, mg/100 ml,

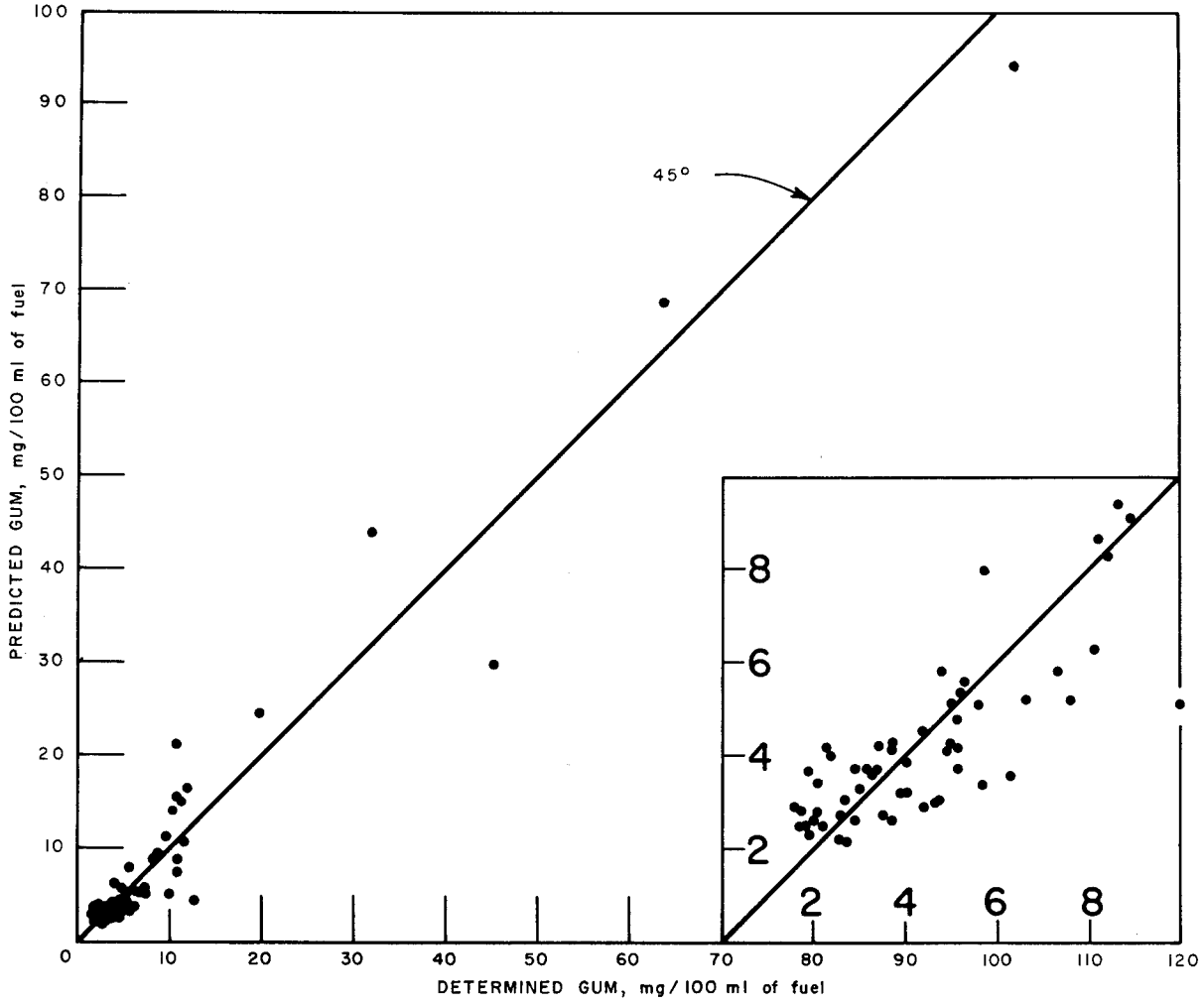


Figure 8.—Comparison of predicted and determined amounts of gum.

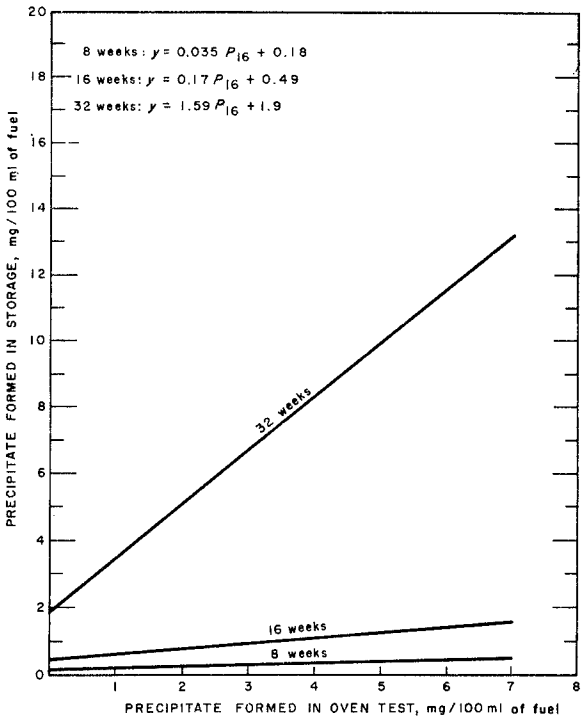


Figure 9.—Relationship of precipitate formation during storage and oven tests.

m = slope of line relating amount of precipitate formed in the oven test to amount formed during each storage period,

and P_{16} = constant equal to average intercepts for precipitate lines.

Values of m and equations for the various periods were developed in the same manner as for the gum equations, with one exception: So much precipitate formed in fuel 9 that these data were considered outliers, and they were omitted from the statistical handling of the data. Figure 9 presents the graphs of precipitate amounts from the storage- and oven-stability tests, for the various storage periods. The slopes of the precipitate lines were plotted against storage intervals, and these are also shown in figure 7. When slope values were read from the line and an average 0.9 intercept was used in the general equation, the following equations were obtained for predicting precipitate formation:

8 weeks at 110° F: Lead precipitate = 0.04 (P_{16}) + 0.9
16 weeks at 110° F: Lead precipitate = 0.14 (P_{16}) + 0.9
32 weeks at 110° F: Lead precipitate = 1.72 (P_{16}) + 0.9

Similarly, the precipitate equations were used to calculate the predicted precipitate formation in each of the 24 gasolines after storage for 8, 16, and 32 weeks at 110° F. The predicted and determined values are compared graphically in figure 10.

The determined values and the corresponding predicted values of gum and precipitate were treated as pairs statistically (*17*) to learn whether they differed. In the treatment, the quantities $\overline{X}_d$, s_d, t, and u were developed as presented in table C–8. The "statistical u" test was then applied and from this, the conclusion (listed in table C–9) was drawn that on the average, the determined values of gum for 8, 16, and 32 weeks of storage and precipitate for 16 and 32 weeks do not differ from predicted values. However, the "statistical u" test indicated that the determined 8-week precipitate data do differ, on the average, from those predicted by the correlations. The value of n is 23 rather than 24 because data from fuel 9 were considered outliers in the statistical treatment.

Development of Prediction Nomographs Based Upon the 16-Hour Oven Test

In some locations it is necessary to store gasoline for an extended period and it is desirable to know in advance the maximum permissible storage time before replacement is needed. To facilitate estimation of this time, data from the oven test were used to develop equations and curves for predicting the storage time needed for a gasoline to form predetermined amounts of gum or lead precipitate. Since the equations were developed to estimate the amounts of gum and precipitate formation rather than total values, it was necessary to consider the initial gum and precipitate levels. Nomographs were prepared for making these estimates, and the steps undertaken in developing these equations are shown below:

Using the equation $G_{110} = m\,(MF_{16}) + G_o + C$, for general gum prediction and previously defined, a modification was developed as follows:

$$\log MF_{16} = \log G_{110} - \log a - (b \log e)\, t \qquad (4)$$

where t = time of storage at 110° F, weeks,
a = constant,
b = constant,
and e = logarithmic base e.

Using this final form of the equation, values for G_{110} were assigned and corresponding values for MF_{16} were calculated for three storage time periods—8, 16, and 32 weeks. Applying an inverted logarithmic scale for the calculated MF_{16} values and a linear scale for t (weeks of storage at 110° F), a nomograph was constructed by

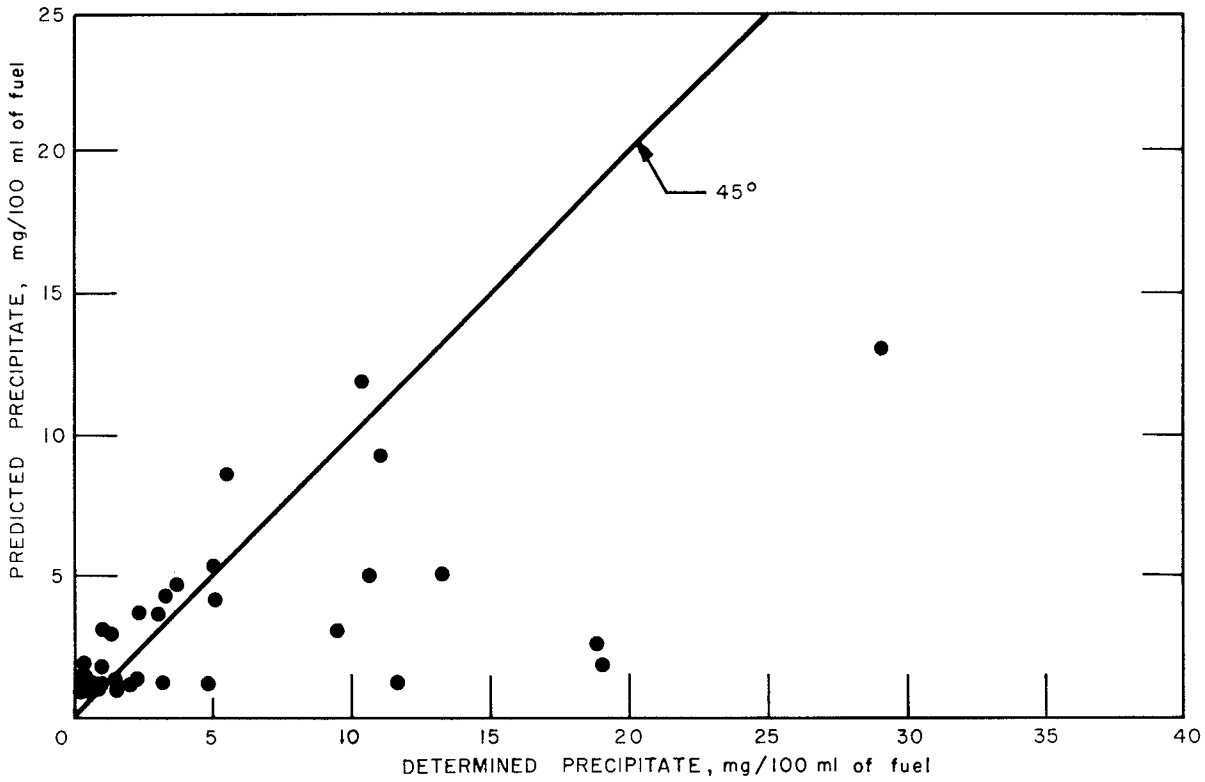


Figure 10.—Comparison of predicted and determined amounts of precipitate.

Table 4.—*Comparison of predicted deposits using the 16-hour oven test and 110° F storage data*

Fuel	Time for 7 mg/100 ml gum, weeks		Time for 2 mg/100 ml precipitate, weeks	
	From nomograph	From extrapolation or interpolation of 110° F storage data	From nomograph	From extrapolation or interpolation of 110° F storage data
1	25	21	23.5	11
2	15	16	27.5	17.5
3	0	0	25.5	24.5
4	29	32	36.5	39
5	23	22	19	18.5
6	22	32	36	33
7	17	15	25.5	29
8	20	16	26.5	42
9	15	6	15.5	1
10	18	16	23	22
11	22	24.5	23	16
12	12	13	29	17
13	54.8	52	34.5	42
14	30	42	31.5	37.5
15	33	20.1	39.5	31
16	[1]	60	39.5	38
17	26	27.5	23.5	24
18	22	24	19	21
19	26	27.5	24.5	24.5
20	21	24	16.5	18
21	29	41	26.5	34
22	22	24	23	21
23	48.8	50	36.5	46
24	35	38	36.5	>52

[1] Not determined.

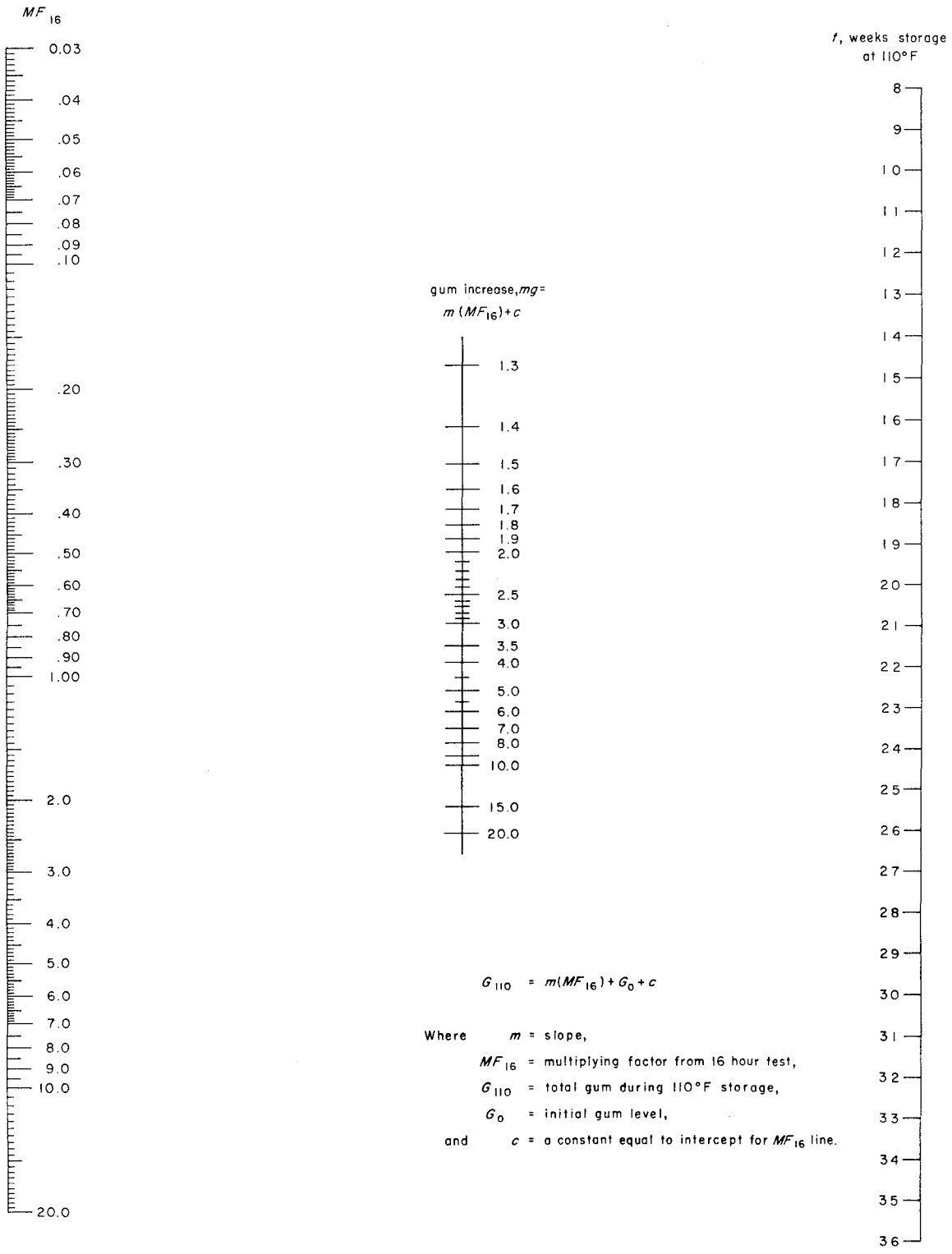


Figure 11.—Nomograph for estimating time in 110° F storage to reach a selected gum increase.

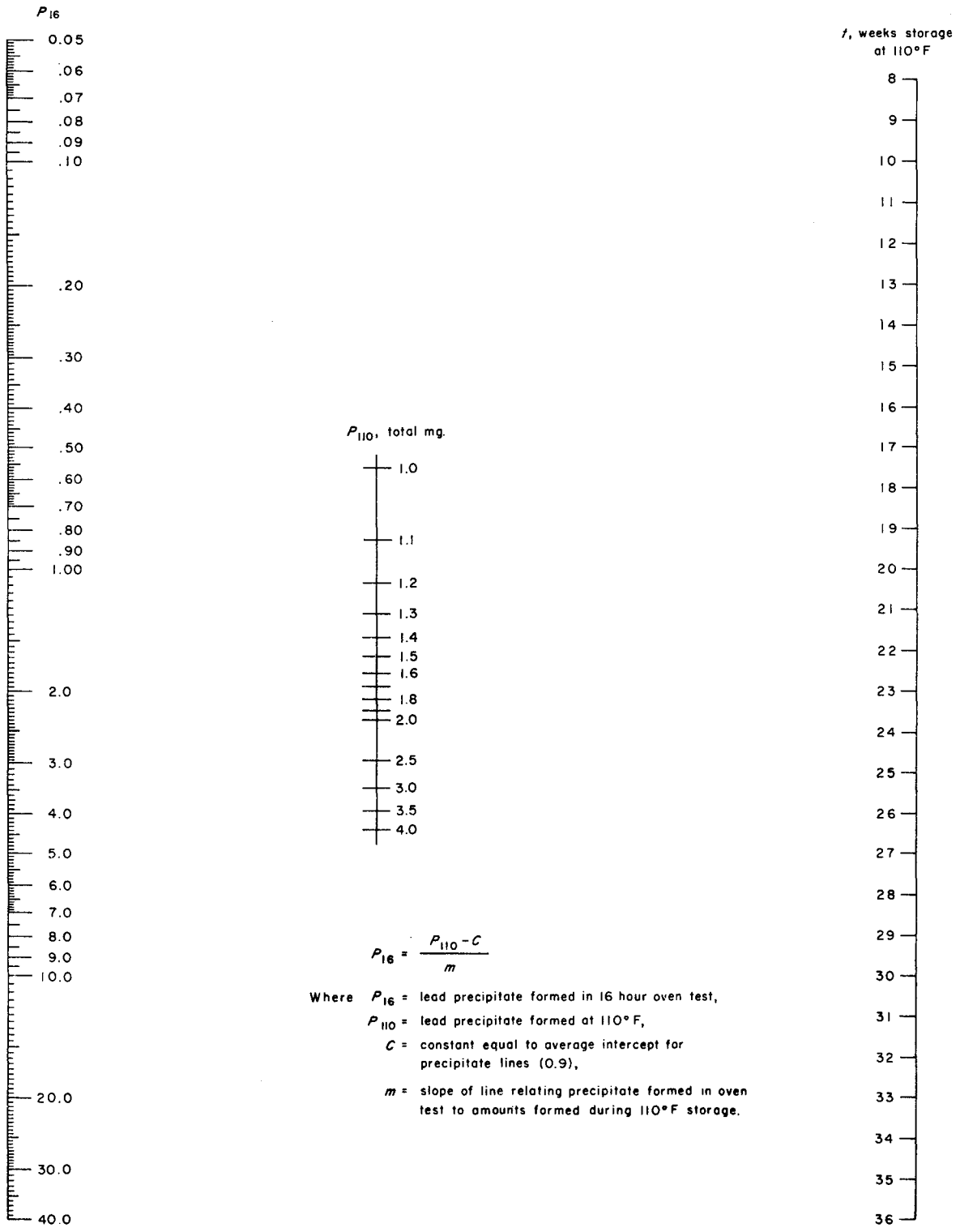


Figure 12.—Nomograph for estimating time in 110° F storage to reach a selected lead precipitate increase.

lining up the corresponding MF_{16} and t values. A vertical scale was constructed for G_{110} values through the points where the three pairs of MF_{16} and t values intersected. This nomograph can be used to determine at what time in 110° F storage any predesignated amount of gum will be formed on the basis of the 16-hour oven test. These gum values are for gum increase, and if total gum values are used as a criterion, the initial gum must be subtracted from the preselected gum value before using the nomograph. The nomograph can also be used in reverse to predict the amount of gum that will be formed in a given length of 110° F storage. In testing these equations, comparisons were made between predicted time t for 7.0 mg/100 ml gum and the approximate values obtained from actual 110° F storage. These values are tabulated in table 4.

Procedure for Use of Nomographs

Figures 11 and 12 show the nomographs developed for predicting total gum and precipitate. To use the nomograph for predicting total gum, the first step is to calculate MF_{16}. This value is obtained from data acquired from the 16-hour oven test and is calculated as follows:

$$MF_{16}=\frac{\text{pct } O_0-\text{pct } O_{16}}{\text{pct } O_0}(G_{16}-G_0) \quad (5)$$

where G_0 = quantity of gum obtained prior to the 16-hour oven test, mg/100 ml,
G_{16} = quantity of gum obtained after the 16-hour oven test, mg/100 ml,
O_0 = 21 pct,
and O_{16} = oxygen in the bottle after the 16-hour oven-test, pct.

With the multiplying factor (MF_{16}), the nomograph shown in figure 11 can be used in either of two ways: First, it can be used to predict the time required (in 110° F storage) to reach any level of gum. Secondly, it can be used to predict the total gum that will be formed in t weeks of storage at 110° F. The initial gum level must be considered in either determination. For example, if the initial gum level is 2 mg/100 ml and the time required for a total of 7 mg/100 ml is sought, then the investigator must place a straight edge across the points corresponding to the calculated MF_{16} and 5 mg/100 ml of gum (7–2) to read the time, t, to reach this level. On the other hand, if the amount of gum that will be formed at 16 weeks is sought, the gum increase read from the nomograph must be added to the initial level in order to obtain total gum at time, t.

If the range covered by the nomograph is not sufficient, values may be calculated as follows:

1. Obtain MF_{16} as described above.
2. Obtain the slope, m, from the curve in figure 13. The values most commonly used are as follows:
   t (8 weeks) $m=0.23$
   t (16 weeks) $m=0.78$
   t (32 weeks) $m=9.15$
   $C=1.2$
3. Substitute the proper values into the general equation

$$G_{110}=m\,(MF_{16})+G_0+C \quad (1)$$

These terms have all been defined in this section.

To use the nomograph shown in figure 12 for predicting the total precipitate formed in 110° F storage from the 16-hour oven test, the total lead precipitate formed in the 16-hour oven test is the only value required. To calculate the same information the following equation is used:

$$P_{110}=m\,(P_{16})+C, \quad (3)$$

where P_{110} = lead precipitate formed at 110° F,
m = slope of line relating precipitate formed in the 16-hour oven test to amounts formed during 110° F storage (See curve in figure 14. The values commonly used are
t (8 weeks) $m=0.04$
t (16 weeks) $m=0.14$
t (32 weeks) $m=1.72$);
$C=0.9$;
and P_{16} = lead precipitate formed in the 16-hour oven test.

Table 4 includes a comparison between the predicted and determined times for gasolines to form 2 mg/100 ml of precipitate.

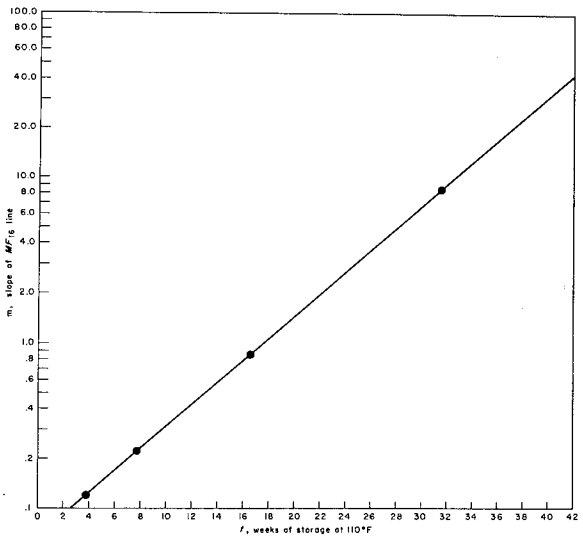


Figure 13.—Relationship between gum line slopes and storage periods.

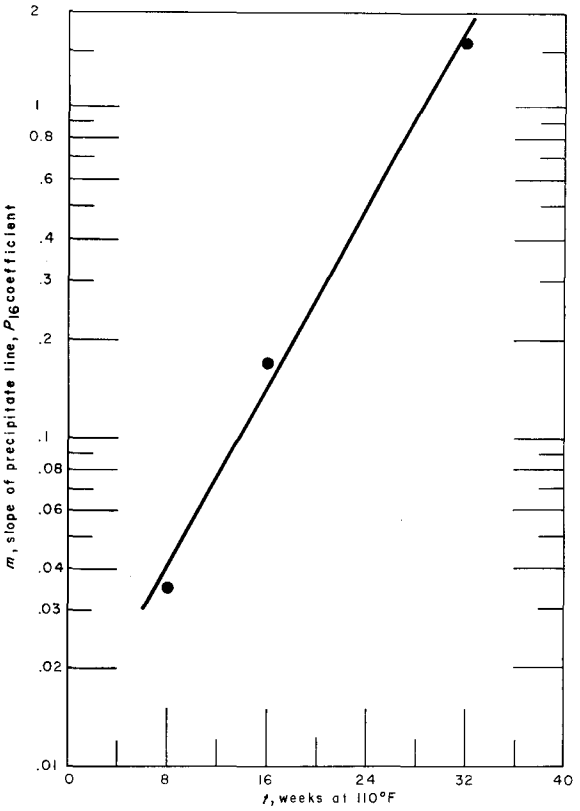


Figure 14.—Relationship between precipitate line slopes and storage periods.

Applicability of 16-Hour Oven Test to Unleaded Fuels

In the development of the prediction test upon which the preceding nomographs are based, a series of 24 fuels were used. Each contained lead alkyl additives ranging from 1.3 to 4.0 g/gal. The selection of fuels containing tetraalkyllead was not accidental, considering prior failures of predictive tests to recognize the detrimental effect of additives in some fuels. However, the question regarding the applicability of the accelerated oven test for stability to unleaded gasolines required investigation. Therefore, four unleaded gasolines were acquired for further study of the accelerated predictive test. Three of these were prototype gasolines used in research on atmospheric pollution by automotive fuels. The fourth was a white gasoline of the type used in lawnmowers.

Initial tests, including air-jet gum determinations, were performed on aliquots of each unstored fuel, and portions of each were then stored at 110° F. The standard storage and aeration procedure was used. Each fuel was also run by the accelerated oven test (16 hours at 200° F). Stored aliquots were removed and tested after 16 weeks.

Table 5 contains the experimental data obtained on these four unleaded gasolines plus the predicted total gum. As can be seen, total gum predictions based upon the 16-hour oven test results were good to excellent for all four unleaded fuels. Although these four gasolines do not represent sufficient data for a statistical evaluation of precision, they do indicate that the predictive test is applicable to both leaded and unleaded fuels, and considerably more reliable for all types of gasolines than the D525 induction bomb test presently used for predicting stability characteristics.

Table 5.—*Prediction data for unleaded fuels*

Fuel	Storage period at 110° F				Predicted	16-hr oven test at 200° F	
	0 weeks		16 weeks				
	Total gum, mg/100 ml	Precipitate, mg/100 ml	Total gum, mg/100 ml	Precipitate, mg/100 ml	Total gum, mg/100 ml	Total gum, mg/100 ml	O_{16} (oxygen), pct
488	2.3	0	3.0	1.6	3.5	3.0	20.9
489	1.2	.11	1.7	.11	2.4	1.9	20.9
490	7.6	.04	9.0	.11	8.8	7.9	20.6
491	1.4	.04	1.7	2.1	2.6	1.2	20.9

FUEL COMPOSITION AND FUEL COMPONENT REACTIVITY AS RELATED TO GUM-FORMING MECHANISMS

Nixon (*18*) has made a comprehensive study of autooxidation and antioxidants of petroleum and has shown that the composition of the gasoline has a considerable effect upon the oxidation stability as well as upon the fuel's response to antioxidants. Sweetening processes or other treatments, such as clay percolation, hydrotreating, catalytic reforming, and additives, can alter or retard the reactivity of gum-forming components of motor gasoline, but a basic knowledge of the reactivity of individual components is essential to an intelligent approach to refinery treatment.

Earlier research by Bureau scientists (*37*) proved that the formation of gum in stored gasolines was related to the reaction of sulfur and nitrogen compounds with different types of unsaturated hydrocarbons. A phase of subsequent work, therefore, was to store certain components of gasoline under laboratory conditions at 110° F, so that the reactivity of selected fuel components could be determined.

A second phase dealt with composition of gum derived from simple three-component mixtures of hydrocarbons and a gas chromatographic (GC) analysis of full-boiling-range gasolines and selected blending stocks with efforts to develop a GC gum determination method.

The final phase of these studies dealt with the reactions of tetraethyllead with pure hydrocarbons and in full-boiling-range gasolines. These subjects are treated in this order in subsequent discussions.

REACTIVITY OF SULFUR COMPOUNDS AND HYDROCARBONS

Materials and Apparatus

A radiotracer technique developed and used in previous research (*37*) was again employed to obtain a quantitative measurement of the gum-forming reactions of specific labeled compounds in 110° F storage tests of selected hydrocarbons and sulfur compounds in the gasoline boiling range. The selection of compounds for investigation included the following materials:

Hydrocarbons	*Sulfur compounds*
Hexene-1	Thiophenol
Cyclohexene	1-Hexanethiol
1, 5-Hexadiene	*n*-Butylsulfide
1-Phenylbutene-2	Thiacyclopentane
2-Methylnaphthalene	*n*-Butyldisulfide
Tetralin	
Indan	

In separate blends, each of the sulfur compounds labeled with ^{35}S or ^{3}H was tested with each of the hydrocarbons labeled with ^{3}H or ^{14}C in an *n*-heptane base. The proportions of components in the blends were 0.5 volume-percent labeled sulfur compound, 24.5 percent labeled hydrocarbon, and 75 percent normal heptane. Each blend was stored in glass bottles at 110° F for periods up to 64 days. The extent of reaction of sulfur compound and hydrocarbon was measured at intervals by vapor transfer (vacuum distillation), gum recovery, and radioactive counting techniques. These data provided a measure of the reactivity of the mixture being tested.

The amounts of reaction occurring were calculated on the basis of the amount of radioactivity in the recovered gum compared with the average radioactivity measurements for each isotope in the blend before gum recovery. The analytical method for determination of radioactivity in blends and gums is detailed in section C of appendix A.

Radiotracers

Compounds labeled with ^{35}S and ^{14}C were purchased from commercial sources. The ^{3}H-labeled compounds were prepared by the Bureau. All of the labeled compounds were purified by appropriate techniques immediately prior to use as tracers.

Blending

Each blend consisted of a labeled hydrocarbon and a labeled sulfur compound in an *n*-heptane base. Each blend was divided into aliquot portions and each aliquot was stored in a separate bottle. The initial gum separation was made on an aliquot immediately after the blend was prepared, and storage was begun on the remainder.

Storage

All of the storage tests were made in 22-oz amber glass bottles, with each bottle containing 200 ml of the blend being tested. The bottles were sealed until removed for gum separation and activity determinations. One 200-ml aliquot was used for gum separation and radioactivity distribution measurements on each blend for each storage period.

Gum Separation

Radioactivity measurements for each isotope present were made on gum recovered by vapor transfer of the sample. This fraction of the total amount of radioactivity for that isotope in the sample determined the percentage of the labeled compound reacted to gum.

Reactions With Thiophenol

A mixture of hexene-1 and thiophenol was stored for 64 days at 110° F. This was the most reactive hydrocarbon with thiophenol. The isotope labels used were tritium (^{3}H) on the sample of hexene and ^{35}S on the thiophenol. It was noted that the two compounds reacted in a proportion of about two parts hexene to one part thiophenol. This may be some indication that the thiophenol molecule acts as a bridge between two molecules of hexene to form gum. The reaction of thiophenol in this mixture was quite rapid, reaching a plateau after about 8 days of storage. This leveling off appears to be a characteristic behavior of thiophenol in most of the blends.

Reaction of a mixture of thiophenol and 1,5-hexadiene was at a somewhat lower rate than that of the thiophenol-hexene blend. The reaction of thiophenol was not as rapid in this mixture as in the previous one, but the reaction plateaued at about the same value. It appeared that approximately equal molar quantities of hexadiene and thiophenol were reacted.

The reaction of cyclohexene and thiophenol in a heptane base reached about half of the value noted in the previous two blends. There was a tendency for the rate of reaction to level out, although it appeared to reach the limiting value at the end of the 32-day storage period.

Data obtained from the thiophenol-1-phenylbutene-2 blend indicated a different kind of reaction. The thiophenol ceased reacting after 18 percent of the thiophenol (corresponding to 1 millimole/100 ml) had combined. The phenylbutene appeared to approach a limit of about 7 millimoles reacted per 100 ml.

Reaction of tritium-labeled indan and thiophenol-^{35}S in a heptane base appeared to be of the same general type as the reaction with phenylbutene. The thiophenol reaction stopped after between 1 and 2 millimoles per 100 ml had reacted. Indan followed the same general pattern: a rapid initial reaction and then a leveling off. However, approximately eight times as much indan was reacted as thiophenol.

In the reaction of tetralin and thiophenol in the heptane base, a relatively slight reaction of thiophenol was noted, with a peak value of around 8 percent reacted in 32 days. Throughout the 32 days, less than 1 millimole of thiophenol was reacted to form gum. A larger quantity of tetralin reacted to gum, up to a 6-millimole-reacted level, which it maintained through the 32-day storage period. This may be some evidence that in the case of tetralin, oxidation forms some intermediate materials that may be recovered as vapor transfer gum.

Of the seven mixtures containing thiophenol, the mixture of ^{35}S-labeled thiophenol with tritium-labeled 2-methylnaphthalene was the least reactive, and reaction of both the hydrocarbon and thiophenol was at a low level in this blend. A larger amount of the hydrocarbon was reacted than thiophenol by a factor of 10.

In figure 15, data are plotted for the reaction of thiophenol in mixtures containing each of the hydrocarbons. This comparison enables a rating of thiophenol in order of reactivity with several hydrocarbons. In general it would appear that olefinic or unsaturated compounds react to the highest extent with thiophenol, and that polycyclics of the tetralin or naphthalene type react to a lesser extent. This figure shows some evidence to support the hypothesis that there are rapid and slow reactions, both of which contribute to gum formation. The rapid type of reaction is shown by the curves for hexadiene, hexene, cyclohexene, indan, and phenylbutene. The slower type of reaction is illustrated by the reaction with tetralin and naphthalene.

Reactions With 1-Hexanethiol

The reactions of the selected group of hydrocarbons with 1-hexanethiol are discussed below:

In the mixture of hexene-1 with 1-hexanethiol, tritium was used as a label on the hexene, and the hexanethiol was labeled with ^{35}S. Neither of the reactants showed much reaction through the 64-day storage period. This was somewhat surprising, since hexene proved to be the most reactive type of hydrocarbon in the presence of

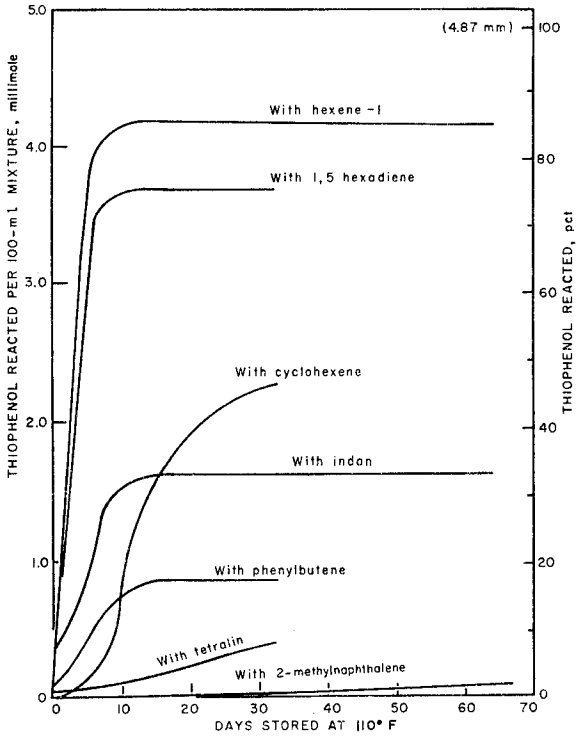


Figure 15.—Reaction of thiophenol with selected hydrocarbons.

thiophenol. The reaction of the hydrocarbon and the sulfur compound was near the same level—less than 0.05 millimole reacted per 100 ml of blend.

A blend of 1,5-hexadiene-^{3}H and 1-hexanethiol-^{35}S was subsequently studied, and it was one of the few mixtures that showed signs of an induction period. The reaction continued at a relatively low level until the end of the 14-day period, when it increased. At the end of 64 days, approximately three times as much hexadiene as hexanethiol was reacted to form gum.

A mixture of cyclohexene-^{3}H and 1-hexanethiol-^{35}S showed a much lower level of reactivity than noted in the blends of thiophenol. In this mixture, evidence of relatively rapid reaction of cyclohexene was noted, with the reaction ceasing after 1 millimole had reacted. The hexanethiol reaction was of somewhat lower level, but it too showed the leveling tendency noted in the other curve.

In reaction of tritium-labeled 1-phenylbutene-2 and ^{35}S-labeled 1-hexanethiol, it appeared that approximately four times as much hydrocarbon was reacting as sulfur compound. The phenylbutene rose rapidly to about a 6-millimole-reacted level and then remained at this amount through the 64-day storage period. The hexanethiol reacted to about a 1.5 millimole/100 ml, and then it too was constant throughout the remainder of the 64-day storage. Phenylbutene proved to be one of the more reactive hydrocarbons when blended with hexanethiol.

In the reaction of tritium-labeled indan and ^{35}S-labeled 1-hexanethiol in a heptane base, there was some parallel between the reaction of thiophenol and indan and the reaction of indan with hexanethiol. There was a relatively small amount of hexanethiol and thiophenol reacted, and by far the largest contribution to gum came from the indan. The hexanethiol reaction was at a very low level and showed a slight increase through the 64-day period to less than 0.01 millimoles/100 ml at the end of 64 days. The indan contributed largely to the gum but was still at a low level as it approached 0.3 millimoles at the end of the 64-day period.

The reaction of tritium-labeled tetralin with ^{35}S-labeled 1-hexanethiol was similar to the behavior of tetralin with thiophenol, although the level of reaction was considerably lower. Hexanethiol reacted to a small extent, approaching about 0.2 millimole/100 ml at the 64-day storage period. By far the largest contribution to gum was from tetralin, and again this may have been caused by oxidation of the tetralin. It approached a value of about 4 millimoles reacted per 100 ml at the end of 64 days of storage.

In the mixture of 2-methylnaphthalene and 1-hexanethiol, the methylnaphthalene was labeled with tritium and the hexanethiol with ^{35}S. This was one of the least reactive mixtures with hexanethiol, and the behavior was similar to that of naphthalene with thiophenol. The contribution from the sulfur compound was quite low, and the methylnaphthalene exhibited a tendency to form more and more gum as the storage time was increased. It reached a value of about 0.3 millimoles/100 ml at the end of 46 days, but the rate was increasing, indicating continued acceleration with longer storage.

The reactivity of this group of hydrocarbons with 1-hexanethiol is summarized in figure 16. The order of reactivity shown in this figure is different from similar data for thiophenol. Only phenylbutene indicated a relatively rapid reaction. The reaction of 1-hexanethiol with all of the other hydrocarbons was slow and at a considerably lower level than the thiophenol reaction. Listed in decreasing magnitude of reaction with 1-hexanethiol, these hydrocarbons are 1,5-

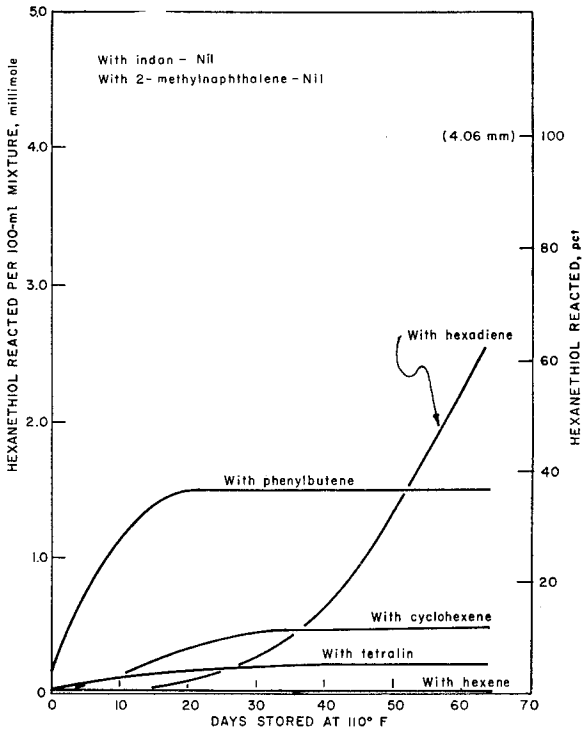


Figure 16.—Reaction of 1-hexanethiol with selected hydrocarbons.

hexadiene, 1-phenylbutene-2, cyclohexene, tetralin, hexene-1, and indan, and at the very lowest level, 2-methylnaphthalene. It is most striking to note that hexene was the most reactive compound when blended with thiophenol, but one of the least reactive compounds when blended with hexanethiol. Otherwise the order of reactivity resembles that of thiophenol in that the olefinic compounds are the most reactive.

Three more series of doubly labeled reaction systems were investigated. These included, first, *n*-butylsulfide-^{35}S with the same labeled hydrocarbon components as in the two previous series. Reactions were consistently low for this series, as indicated by the radiotracer levels as well as by actual gum recovered.

A reaction series of these labeled hydrocarbons combined with *n*-butyldisulfide-^{35}S showed much the same results. The level of reaction was very low, and the disulfide was subsequently classified as quite unreactive in the environment presented.

The third series of radiotracer studies included thiacyclopentane-^{35}S as the sulfur compound in combination with the same labeled hydrocarbons. These reactions, too, were very low, and the systems were classified as relatively unreactive.

A Summary of Reactions of Sulfur Compounds

The preceding data showed two general types of curves, one of which was autoaccelerated; that is, the rate of reaction increased with time. The other curve was autoretardant, approaching the exponential type of curve in which the rate of reaction lessened with increasing time.

In analyzing the data from this work, it was apparent that most fuel deterioration reactions could be represented by some portion of the common S-type curve. The advantages of this type curve over a simple exponential function include allowances for both induction periods and self-inhibiting systems.

In processing these data, a program for fitting the curve by computer was used. It was found that all of the data could be fitted to an exponential equation

$$y=\frac{a}{1+be^{-cx}},$$

where y = amount reacted, x = storage time, a, b, and c are constants, and e is the logarithmic base e.

The relatively unreactive mixtures yielded curves of the autoaccelerated type, but the more reactive mixtures generally showed an autoretardant mixture.

The possibility of using the reactivity of thiophenol to predict storage stability was studied with a group of labeled gasolines. Data presented in table D–1 show that no correlations exist between percent thiophenol reacted and the stability of the fuel in terms of gum formed during storage.

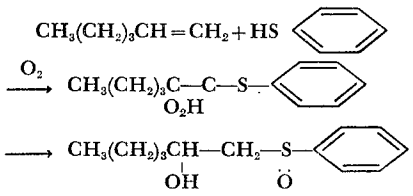
GUM ANALYSIS

Stanford Research Institute of Palo Alto, Calif., was a cooperator in gasoline stability studies prior to 1960. The work of that research organization dealt primarily with gums and included elemental analysis, determination of the physical characteristics, functional group analysis, molecular-weight determinations, examination by infrared, ultraviolet, and mass spectral procedures, determination of nuclear magnetic resonance spectra, and saponification studies. In brief, the SRI study of gum resulting from accelerating the degradation of motor gasolines was quite comprehensive. At the termination of its studies, SRI had embarked upon a limited

study of reactions occurring in two- and three-component synthetic blends of hydrocarbons. Because these studies were of particular interest, they were continued by the Bureau in a study somewhat less comprehensive in scope.

Elemental Analyses

Elemental analyses and molecular-weight determinations were made for the vapor-transfer gums recovered from several three-component blends that had been stored at 110° F with periodic air replenishment. These analyses are listed in table D–2. No nitrogen determinations were made, since this class of compound was not included in the mixtures. These elemental analyses showed that sulfur content ranged from 0.3 to 15 percent. Oxygen content of the gums varied, with some as high as 16 percent. Estimating the molecular composition of the average gum was possible, assuming that the entire sulfur compound molecule was incorporated in the gum. Three of the gums studied appeared to be of the type reported by Oswald and Ruper (*19*). Their study indicated that thiols and olefins readily cooxidize to form unstable peroxides, which rearrange to form the corresponding hydroxysulfoxides. For example, a mixture of 1-hexene and thiophenol reacts with oxygen as follows:



The resulting hydroxyhexylphenylsulfoxide has an empirical formula of $C_{12}H_{18}SO_2$ and a molecular weight of 226. Similar reactions might be expected of the 1,5-hexadiene and the cyclohexene. Assuming that this cooxidation is the major reaction, the calculated elemental analysis and molecular weight of this type of structure are shown in table D–3 and compared with actual analysis of the gums. The agreement is excellent for mixtures shown in group I, and postulated structures are the dominant products.

The mixtures shown in group II of table D–3 were less definitive in final analysis. A molecular formula was developed based upon available data and some assumptions regarding the nature of the gum molecule. These are shown in table D–3. The fractional atomic notations of sulfur and oxygen in molecular formulas for these gums point towards a heterogeneous mixture of oxidized material with reaction products of sulfur.

Mass Spectrometer Analysis of Gums

Mass spectrometer analysis of the nonvolatile residues from vapor transfer of the six ternary blends shown in table D–2 showed evidence for several types of reaction products.

Generally speaking, the mass spectra of the residues from the five thiophenol blends were characterized by the presence of ions at masses corresponding to the oxidation of thiophenol and to the disproportionation of its oxidation products. This resulted in ions of masses corresponding to biphenyl, phenyl-(sulfide, disulfide, sulfoxide, sulfone, and disulfoxide), or fragmentations from them. In addition, peaks were found that corresponded to oxidation of the hydrocarbon present to form oxidation products having from one to five oxygen atoms. Finally, ions were found corresponding to a union of free radicals from the hydrocarbons and their oxidation derivatives with each other and with free radicals derived from thiophenol.

Some evidence of polymerization was found for the 1-hexene and 1,5-hexadiene blend residues, but primarily the products were cooxidation products with thiophenol-derived free radicals. The postulated structures in table D–3 are, in each case, one of these types. Other peaks suggest a similar product having either a hydroperoxide or keto group added to the chain or oxygen added to the sulfur atom to give the sulfone. Finally, derivatives were found which corresponded to replacement of the phenyl sulfoxide group with a phenyl or phenyl sulfide group in the postulated structure.

Similar compound types were found in the cyclohexene blend spectrum, but evidence for carbon-carbon bond condensation of the olefin and its oxidation derivatives with each other was more pronounced. Also, the spectrum suggested that multiple-oxygen attack on the ring occurred. This was reasonable since formation of the α ketone yields a free radical stabilized by resonance between the keto and ring double bonds. This radical is more susceptible to polymerization and to further oxidation because the activity of the β-methylene group is enhanced.

Formation of the α-ketone of tetralin gives a structure in which the keto double bond is conjugated with the aromatic ring. This can give rise to a free radical of still greater stability and also impart activity to the β-methylene group. Ions representing unions of tetralin and

its oxidized derivatives with thiophenol-derived free radicals were abundant.

1-Phenylbutene-2 has a methylene group α to the ring and to a double bond that spreads the resonance of the free radical over all of the atoms and hence decreases its reactivity. In addition, more than one hydroperoxide isomer can be formed, and since some of these have conjugated double bonds, both carbon-carbon bond and peroxide bonded polymers can form. (This mechanism is analogous to that for drying oils containing linoleic or linolenic acid.) The physical appearance of these gums (very viscous semisolids) also suggests polymerization solidification. Ions were found corresponding to from one to eight oxygen atoms in the spectra, but since the most abundant of these have from three to five oxygen atoms, it seemed that these more than likely represented the units of the polymers formed. Those with more than five oxygen atoms represented either less prevalent polymer types or fragments formed from less probable cleavages of the three to five oxygen atom polymers by electron bombardment. Presence of phenylpropyl radicals in the spectra may come from polymer cleavages, or possibly from loss of CH_2OH from the one primary alcohol that can form from oxidation of 1-phenylbutene-2.

In the residue of the 1-phenylbutene-2 and thiophenol blend, evidence was abundant for compounds formed by union of free radicals derived from both compounds and their oxidation derivatives.

In the residue of the 1-phenylbutene-2 and thiacyclopentane, evidence was found for oxidation of thiacyclopentane. There was also evidence of cooxidation products formed from 1-phenylbutene-2 and thiacyclopentane-derived free radicals.

Finally, evidence was observed for thermal decomposition, characterized by (1) loss of H_2, (2) cyclization, and (3) formation of double bonds in the ring by successive losses of H_2. This gave ions corresponding to losses of 20 mass units from structures containing the alcohol group, and to benzocyclohexenyl and naphthyl radical derivatives analogous to those formed from tetralin and 1-phenylbutene-2.

Molecular Weight of Gums

One of the questions that required answering pertained to the molecular weight of residue obtained in the vapor transfer (VT) separation as well as the conventional air-jet gum determination. Data pertaining to vapor transfer gum are listed in table D–4. This table shows the amount of material remaining in the vapor transfer distillate and the amount of residue for the listed hydrocarbons. These were run by dissolving about 0.2 gram (100 mg/ml) of the compound in 200 ml of normal heptane and then making the vapor transfer on this mixture.

Also included in this table are results on a four-component mixture consisting of octadecene, hexadecane, tetradecane, and dodecene. These data show that materials with a molecular weight of 200 or less transfer with the distillate, and that those above 200 remain as a residue.

Similar tests were made with the air-jet gum evaporation method using hexadecane, nonadecene, docosane, tetracosane, and octacosane. These results are shown in the same table, and it is evident that the minimum-molecular-weight material showing up as air-jet gum would be about a C_{20} with a molecular weight near 300. Generally speaking, the molecular-weight range of VT residues extends to lower values than those of air-jet gums. This result of the study was anticipated but did not obviate the value of vapor transfer for certain investigations.

GAS CHROMATOGRAPHIC ANALYSIS OF GASOLINES

Gas chromatographic analysis of fresh and aged gasolines was first explored as a technique for showing and defining major differences in fuel composition as a result of oxidation and degradation occurring during storage at 110° F. Comparative analyses were made using high-boiling substrates in both packed and capillary columns of various lengths. The procedure that was adopted as best suited for these studies used a 500-ft capillary column with a high-boiling nonpolar substrate. Exhaustive analyses were confined to fresh and aged portions of one fuel (BOG–202). Differences between fresh and aged gasolines were noted in several boiling ranges of this fuel. However, by a series of separations performed on both polar and nonpolar substrates at various temperatures, several peaks were trapped for analysis by infrared and mass spectroscopy. Two materials, which during the aging process appeared to be changing according to differences noted in chromatograms, were identified as either cycloolefins or diolefins. Microhydrogenation combined with mass spectra showed these to be dimethyl- and trimethylcyclopentane. It was noted that about 88 percent

of the cycloolefin disappeared during the storage at 110° F. Analysis of the fresh gasoline with 0.5 percent of 1,2-dimethylcyclopentene added as a spike verified the identity of this material by retention time, but also permitted calculation of the quantity of this olefin present in the original gasoline. By storing an aliquot of this blend containing the cycloolefin spike, it was shown that the added material reacted to the extent of 41 percent in 10 weeks. Using a packed column to permit larger samples for trapping resulted in the separation and identification of several reactive olefins in this gasoline, including cyclopentene, methylcyclopentene, 1,2-dimethylcyclopentene, 1,2,3-trimethylcyclopentene, 1,2,4-trimethylcyclopentene, 1-methyl-2-ethylcyclopentene, 1,3-dimethylcyclohexene, 2-methyl-3-hexene, and isopropenylcyclopropane.

Studies of yet another gasoline (BOG–295) led to the positive identification of only one reactive component: 2,3,4-trimethylpentene.

Although these studies were rewarding insofar as time and personnel permitted, it was apparent that to analyze even one gasoline completely by this technique would require much more time than could be allotted to the investigation. However, as an offshoot of this study, it was noted that very-high-molecular-weight material, as indicated by a long retention time, was eluted from the chromatographic column at elevated temperatures. This suggested that these materials were probably oxygenates or polymers resulting from aging and thermal stress of the fuel and that they might be correlated in quantity to the gum. Further studies were necessary to evaluate the usefulness of this technique as an analytical tool for gum determination.

GAS CHROMATOGRAPHIC ANALYSIS OF GUMS

The backflush technique that was developed evolved from results obtained on an initial study shown in table D–5. This table lists the samples that were analyzed, the air-jet gum concentration, expressed in milligrams per 100 ml and in parts per million for comparison. The other columns in the table list in parts per million the quantities of high-boiling material obtained by chromatographic analysis. Data in the first column were obtained with a 72-minute forward flow and no backflush operation; the second column shows the GLC peak in parts per million as determined using a 16-minute forward flow and then backflushing the column. The third column shows the GLC peak in parts per million obtained using a 72-minute forward flow and then a backflush.

The retention times of several pure compounds obtained with this column are listed in table D–6. Backflushing at 16 minutes included C_{20} and higher materials in the backflush peak. From the retention time table, if the column was run for 72 minutes before backflushing, any material showing in the backflush peak would be higher-boiling than a C_{24} compound. A typical GLC run with a 16-minute backflush is shown in figure 17.

This work offered ample evidence of significant amounts of high-boiling components in gasoline and gasoline stocks which could not have been determined by conventional methods of analysis.

Procedure

GLC runs using a backflush technique were made with a gas chromatographic column operated at 200° C and equipped with a backflush valve and flame detector. An internal standard (n-C_{18}) was used in 0.1 volume-percent concentration, and the amounts in the backflush peaks were calculated by comparison with the standard peak. The full flow of the column was run through the flame detector in order to obtain maximum backflush peak area. The retention time of the internal standard was about 8 minutes, and the column was operated with forward flow for 16 minutes before backflushing. The major portion of the fuels passed through the column in less than 4 minutes. No resolution of the major fuel components was attempted, but definition of the standard peak and backflush peak was good under the conditions described. A sample volume of 20 μl was adopted as a standard charge, after using volumes ranging from 10 to 50 μl.

Results

Table D–7 shows the results of duplicate runs on the same sample and internal standard mix. The data are grouped by peak area, and the standard deviations of the groups are shown. The deviation is about 10 percent of the determined area. This represents the inherent deviation of the method.

Table D–8 lists the results of repeated sampling and internal standard mixes on seven fresh gasoline stocks selected for this work. Standard deviations for repeated determination of the backflush peak areas of these samples are shown. There is a large variation in the magnitude of the peak areas in the different samples.

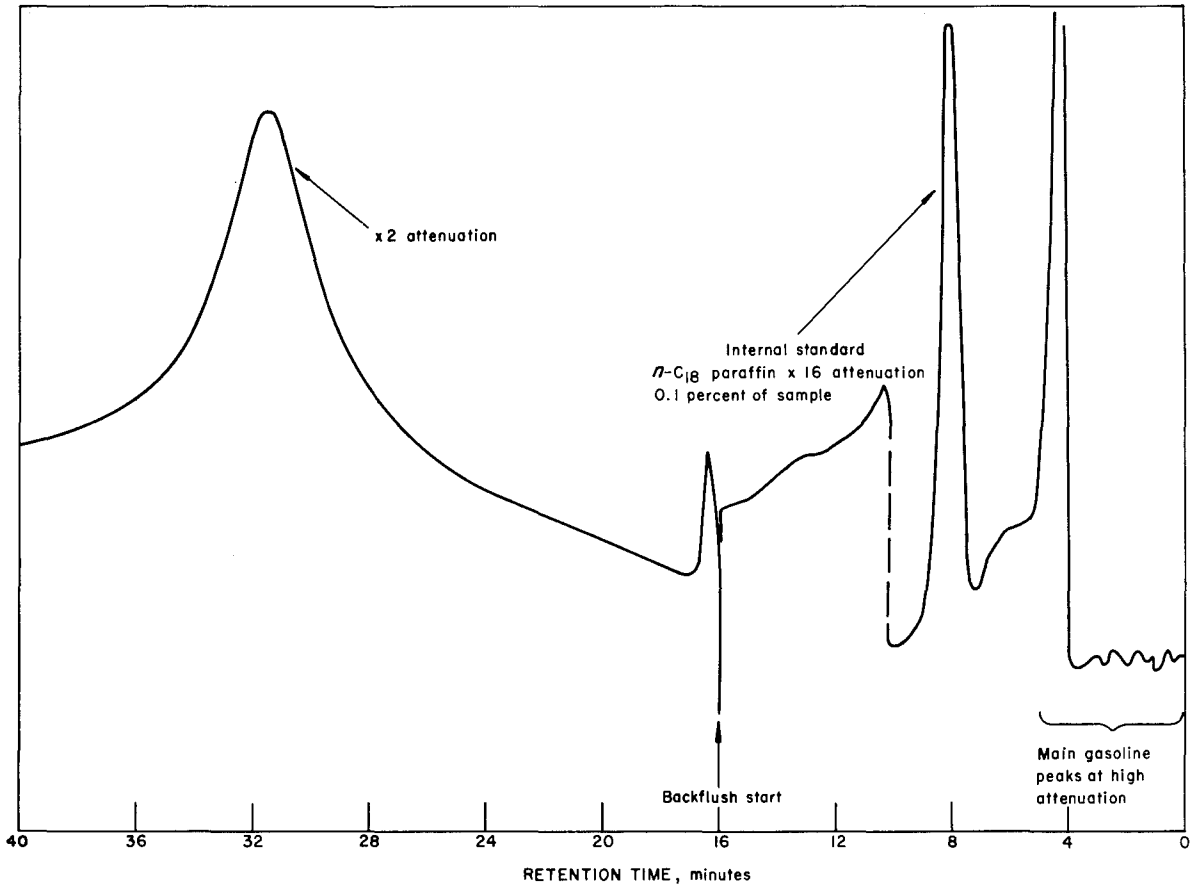


Figure 17.—Backflush peak area, aviation gas blending component (0.0404-percent, 10μl sample).

A comparison of change in backflush peak area and change in total gum content for the first group of fuels aged in bombs is made in table D–9. It is evident that there is no definite relationship between change in peak area, or gross peak area, and the gum content of the sample. A consistent trend towards higher peak areas in the high gum samples may be noted.

The backflush peak areas and gum level for fuels aged at 110° F are shown in table D–10. From these data, as well as from the bomb results, it is evident that there is no fixed relationship between gross peak area or change in peak area with the gum level in the fuels tested, but that for a given fuel the peak area increases with fuel aging. This investigation showed that the backflush chromatographic technique was not satisfactory as an analytical tool for determining gum in gasoline.

TETRAETHYLLEAD (TEL)— HYDROCARBON REACTION STUDIES

Gasoline in long-term storage may become unusable because of excessive gum formation or because of formation of a haze of insoluble fuel compounds caused by reaction of TEL (*13*). The final phase of these investigations was a study of reactions of TEL and hydrocarbons to identify the types of hydrocarbons that react with TEL to form these insoluble precipitates.

It was known that TEL tends toward oxidation (*1, 5, 10, 15, 21–22, 38–41*) and exerts an influence on the activation energy of gum formation reactions in motor gasolines, with the result that leaded gasolines are somewhat less stable than unleaded fuels in normal storage.

Postulated Reaction Mechanisms

Shimonayev and Rozhkov (*38*) showed in 1955 that the mechanism of oxidation of TEL

was initiated by the decomposition of TEL into free radicals:

$$Pb(C_2H_5)_4 \longrightarrow Pb(C_2H_5)_3\cdot + C_2H_5\cdot.$$

The radicals formed from this decomposition are the initial reaction centers of the oxidation, and they might participate in a radical exchange reaction, as follows:

$$C_2H_5\cdot + R\text{–}H \longrightarrow C_2H_6 + R\cdot,$$

and

$$Pb(C_2H_5)_3\cdot + R\text{–}H \longrightarrow (C_2H_5)_3Pb\text{–}H + R\cdot.$$

The ethyl radicals and the radicals formed as the result of the exchange reaction produce peroxide radicals and hydroperoxides on contact with oxygen:

$$R\cdot + O{=}O \longrightarrow R\text{–}O\text{–}O\cdot.$$

and

$$R\text{–}O\text{–}O\cdot + R'\text{–}H \longrightarrow R\text{–}O\text{–}OH + R'\cdot.$$

These finally react with tetraethyllead to form oxygen-containing lead compounds.

The reaction between tetraethyllead and the hydroperoxide was postulated to be represented by the following equations:

$$Pb(C_2H_5)_4 + R\text{–}O\text{–}OH \longrightarrow Pb(C_2H_5)_3OH + R\text{–}O\text{–}C_2H_5, \quad (6)$$

and/or

$$Pb(C_2H_5)_4 + R\text{–}O\text{–}OH \longrightarrow Pb(C_2H_5)_3O\text{–}R + C_2H_5OH. \quad (7)$$

Trialkyl lead compounds are soluble in hydrocarbons, but a further reaction of this compound with the peroxide results in the formation of dialkyllead compounds of the following types: $(C_2H_5)_2\ Pb(OH)_2$, $(C_2H_5)_2\ Pb(OR)_2$, and/or $(C_2H_5)_2\ Pb(OR)(OH)$. These compounds are not very soluble in hydrocarbons and are therefore precipitated.

Under the conditions of the oxidation reaction of hydrocarbons in the presence of tetraethyllead or its decomposition products, it might be assumed that other active compounds which are present in the hydrocarbon could enter into the reaction. Sulfur, halogen compounds present in ethyl fluid, and nitrogen compounds present in the gasoline are likely reactants, and our studies as well as others (*21–22, 40*) have shown one or more of these reactants in lead precipitates.

The reaction of TEL with specific hydrocarbon components of gasoline was of paramount interest in the present study. It was hoped to determine the exact composition of soluble organolead intermediate reaction products and thereby confirm or refute the postulated mechanisms based upon actual storage data of pure hydrocarbons with TEL.

Materials and Apparatus

Blends

Binary hydrocarbon mixtures were selected for study, rather than more complex systems represented by full-boiling-range gasolines. These binary blends were designed to consist of a 0.5-volume-percent reactive hydrocarbon in an inert base hydrocarbon (99.5 percent). To each blend was added a special blend of tetraethyllead fluid that contained halide scavengers but no antioxidants. Ordinarily, the concentration of TEL was 3 $cm^3\ gal^{-1}$.

Preliminary tests were made to find an inert base hydrocarbon and to establish other basic test parameters. Isooctane was selected as the base stock from six compounds tested for blending in binary systems, based upon availability, purity, and low precipitate formation at test temperatures below 200° F. Purification of reactive components was included as a prerequisite to testing and was accomplished using gas chromatographic separations, vacuum distillation (vapor transfer), and adsorption column separations. These methods were used singly or in combination to achieve the best practical purification of each individual reactant. A Beckman preparative-scale GC was employed for purification purposes, and a Perkin-Elmer 900 Analytical GC was used for purity checks. The reactive components for each blend were selected from groups representing the following types of compounds found in gasoline: cycloolefins, diolefins, aromatic olefins, aromatics, chain olefins, and paraffins.

Test Procedures

Blends were oven-tested in beverage bottles at 180° F for 40 hours. Then 130 ml of each test blend was placed in a 16-oz bottle, which was in turn encased in a cylindrical safety shield and placed in an oven maintained at the test temperature. The bottles were capped with a special closure to permit sampling the outage in the bottle for oxygen consumption at the end of the test. Deterioration during the oven test was measured by determination of precipitate, insoluble gum, soluble gum, and oxygen consumption.

The soluble gum, fuel-insoluble gum, and lead precipitate were determined as described in sections A2–A4 of appendix A, respectively. Insoluble gum was dissolved in a trisolvent (benzene, acetone, and methanol) and weighed after evaporation of the solvent.

Percent oxygen in the outage of the bottle at the end of the oven test was determined by using the method described in section A5 of appendix A.

Results

A purification program was undertaken for the reactive components that were to be studied in reaction mixtures with TEL. Table D–11 lists the data obtained from this study. Six runs were made on the isooctane base stock with added TEL. These blends are not binary as the remainder are. If this table were arranged in order of descending lead precipitation, the cycloolefins would be found at the top of the table, followed by diolefins, olefins, and indene, which is an aromatic olefin. The remainder of the table would consist of the paraffins and aromatics, both of which showed little or no tendency toward lead precipitation. Total gum would follow the same general pattern.

It was observed from these data that little or no difference in lead precipitation tendency was apparent among the straight-chain olefin blends. The same was not true for the cycloolefins. A 1,2-disubstituted cyclohexene showed approximately twice the lead precipitation reaction during the test of that of cyclohexene itself. On the other hand, precipitation from the 4,4-disubstituted isomer was only a tenth of that of the parent compound. The 3,3,5-trisubstituted homolog also showed very low precipitate reactions. The largest tendency for lead precipitation was found in the three blends containing homologs of cyclopentene. However, only small differences were observed between the 1,2-disubstituted and the two trisubstituted forms.

Oxidation, which is an integral part of these reactions, most likely occurs on the allyl hydrogen rather than at the double bond itself. With perhaps only one or so anomalies, this explains the high reactivity of some of the cycloolefins tested and the rather low reactivity of straight-chain olefins, indene, indan, and a few of the cycloolefins.

Elemental Analysis of Lead Precipitates

A set of 13 leaded gasolines stored at 110° F for 1 year or more was selected for elemental analysis of the precipitates. These analyses are shown in table D–12, along with the analyses of four precipitates from binary hydrocarbon blends. The average lead in the precipitates from the 13 gasolines stored at 110° F for 1 year was about 55 percent, whereas the oxygen and carbon were near 21 and 20 percent, respectively. On the other hand, the three binary blends stored at 180° F for 40 hours contained more lead—nearly 71 percent. To check the effect of time or temperature, or both, upon this elemental composition, the binary blend containing 1-ethylcyclopentene was stored at 110° F for 5 months and the elemental analyses were repeated. Conversely, one of the 13 gasolines was stored at 180° F in the laboratory oven for 124 hours. The result was that the lead content was definitely affected by temperature and test duration. At lower temperatures, the elemental composition of the lead precipitate from the binary blend was similar to that of the 13 gasolines stored under identical conditions. Conversely, the gasoline precipitate changed in character when higher temperatures were applied, with a resulting precipitate that was similar in composition to that obtained from binary blends. These data suggest quite strongly that the final structure of the lead precipitate is a function of the energy supplied to the reaction system. Therefore, the lead precipitate formed at ambient-temperature storage quite likely differs from that obtained from either of the test conditions of this study. The precipitate formed at 110° F has a molecular weight calculated to be about 375, based upon the average elemental composition, and a general formula of $Pb\ O_5C_6H_8$. This corresponds more nearly to diethyl-carbonate, as shown in table D–12, but the precipitate formed at 180° F has a molecular weight of about 580 and a general structure of $Pb_2O_7C_3H_6$.

X-ray diffraction studies of some of the lead precipitates obtained from these studies showed most to be mixtures. Basic lead carbonate ($2\ PbCO_3 \cdot Pb(OH)_2$) was tentatively identified in the precipitate from 1-hexene. There was some evidence for diethyllead carbonate in several analyzed precipitates.

Soluble Alkyllead Salts

To study the nature of intermediate organolead products, a series of chromatographic separations was made using a preparative-scale, 11-ft by 5/8-in Carbowax 9000 column at 88° C and a hot-wire detector. The eluted sample was collected in three large fractions, each of which was checked with the electron-capture analytical instrument to locate the material containing the probable lead alkyl. These traps were examined by both mass and infrared spectral analysis, but there was no evidence for any halogenated or lead-containing compounds. The spectral data indicated only aromatic hydrocarbon types. It was tentatively concluded that if lead alkyl intermediates did exist in these fractions, they decomposed or were destroyed during processing.

There was some substantiation (*12*) of the instability of these intermediates at temperatures near 100° C or even lower. Bartleson and Shepherd (*10*) reported that trialkyllead oxide, which was considered an intermediate oxidation product of TEL, was quite unstable and therefore difficult to isolate and identify positively. An indirect determination using wet chemical methods (*16*) is probably a superior method of estimating composition of intermediates.

Further studies of soluble alkyllead salts were made on an aged binary blend of leaded hydrocarbons containing cyclohexene. Gas chromatographic analysis using an electron-capture detector showed no unidentified peaks. The interpretation of these data was that soluble lead compounds other than TEL were either absent, below detection limits, or in high-boiling compounds not eluted early enough from this GC system to be observed. However, it was decided to separate and analyze the 29-day storage sample of this blend in much the same manner as described for the gasoline. Several GC traps were collected during preparative-scale separation and were identified by mass and infrared spectra as dibromoethane (a component of the TEL mix) and 2-cyclohexenone, respectively. Although the spectra of other material collected were not identified, they did indicate that oxygenated hydrocarbons were prevalent. The molecular weight of trap 1 was 128, and a *t*-butyl group was evident. Infrared analysis showed both—OH and $-C=O$ functional groups. Trap 2 had a molecular weight of 112 with a fragment at m/e 115 which could have resulted from an alcohol with no definite parent peak. Infrared spectrography also showed hydroxyl groups in this fraction.

In a related study, the spectroscopic examination of materials and products of a reaction mixture containing cyclohexane, isooctane, and TEL showed cyclohexanol to be a component. Therefore, the effect of adding cyclohexanol to a reaction mixture was investigated by preparing two blends of cyclohexane leaded to 20 cm^3 gal^{-1}. To one blend 3 percent cyclohexanol was added; both blends were then stored at 180° F for 10 days, during which time portions were removed and analyzed at intervals. The results showed that the cyclohexanol inhibited precipitate formation because only 64 mg/100 ml was formed in 4 days, as compared with 276 mg/100 ml found in the control sample. Analysis of the blend containing cyclohexanol showed the presence of another alcohol (methanol) and a ketone (cyclohexanone).

Yet another phase of this investigation included three more binary blends that were prepared for further study of alkyllead intermediates to TEL precipitation reactions. All of these blends contained 1-ethylcyclopentane in isooctane base stock. This cycloolefin was the most reactive in terms of lead precipitation of any of those tested. The major difference in the test blends was the TEL content. Two blends (Pb–144 and Pb–168) contained 3 cm^3 gal^{-1} TEL, whereas the other (PB–169) contained 150 cm^3 gal^{-1}. Aliquots of each blend were stored at 180° F and sampled at intervals throughout the experiment by drawing 25 ml through a 0.45-micron cellulose ester filter to remove any precipitated lead products. Table 6 shows the data collected

Table 6.—*Differential lead analyses of aged binary hydrocarbon blends containing TEL*

Sample	Storage time at 180° F, days	Pb as TEL by GC/EC,[1] ppm	Total Pb by ESA,[2] ppm	Difference Ppm	Difference Pct
Pb–144[3]	0	950	950	0	0
	2	390	603	213	35.3
	7	33	29	0	0
	63	3	< 11	--	--
Pb–168[3]	0	916	916	0	0
	1	916	906	0	0
	2	537	764	227	25
	3	483	627	144	16
	7	81	135	54	6
	14	0	0	0	0
Pb–169[4]	0	44,980	44,979	0	0
	2	44,420	44,759	339	.8
	4	40,480	42,741	2,261	5.3
	6	35,315	40,176	4,861	12.1

[1] Gas chromatographic separation with electron-capture detection system.
[2] Emission spectrographic analysis.
[3] Contains 3 cm^3 gal^{-1} TEL.
[4] Contains 150 cm^3 gal^{-1} TEL.

on these materials. These data indicated that the maximum difference between total lead and lead combined as TEL was achieved in 2 days at 180° F if the TEL level was 3 cm^3 gal^{-1}, but the blend that contained 150 cm^3 gal^{-1} TEL showed that the soluble lead alkyls were increasing even at the 6-day storage interval. Insufficient material terminated the latter test before the maximum soluble alkyllead salts (SALS) were achieved.

Walters and Busso (*20*) reported results of aging undiluted TEL fluid at 110° F. In their study they found that after 4 days' storage, the samples contained about 6 percent trialkyllead salts which they determined to be one of the major intermediate decomposition products. The trialkyllead content leveled off at about this value and began to taper off with

further aging. These results were not borne out in our study, which showed as much as 25 percent SALS in one blend, whereas the other reached 12 percent without evidence of leveling off. The difference between these two studies probably lies in the concentration of TEL and the temperature at which accelerated aging was accomplished. The evidence would indicate that higher reaction temperatures not only affect the composition of the final lead precipitate, but also are important in the buildup of soluble lead alkyls.

Bartleson and Shepherd (*10*) found that although there is no reason to believe that the soluble alkyllead salts themselves are deleterious, they are precursors of the undesirable insoluble materials. Their data indicated that the lead precipitate reached an objectionable level when the SALS content was approximately 3 mg Pb/100 ml. Although this was a typical level for most fuels, precipitation occasionally was not appreciable until the SALS level reached 7 to 10 mg Pb/100 ml. Their appraisal was that this was not a simple solubility function related to basic hydrocarbon type, but a result of the complexity of the mixture of organic and inorganic lead compounds and their solubility properties.

Table 7 shows the results obtained by emission spectrographic analysis for total lead before and after extracting two of the samples with dilute nitric acid. Extraction with acid is the first step in the determination of SALS by the method of Henderson and Snyder (*16*). Previous information indicated that the 2-day sample of Pb–168 was about 25 percent SALS as determined by difference between chromatographic analysis for lead as TEL and emission spectrographic analysis for total lead. Differential analysis by emission spectroscopy of this sample before and after extraction with nitric acid indicated 47 percent SALS. This discrepancy could be partly or wholly analytical error and sample degradation during the interval between the two analyses, but it is not of significant concern.

A concentrated effort was made to separate and identify intermediate lead products in the 2-day sample of Pb–168 using a gas chromatograph equipped with an electron-capture detector.

Figure D–1 shows the electron-capture detector response to the materials eluted in the separation of each of three samples. These samples were Pb–168 (*A*) fresh; (*B*) after 3 days' aging at 180° F; and (*C*) after 7 days' aging at 180° F. These chromatographic separations were made at isothermal conditions (100° C). A few peaks found in the fresh sample disappeared after 3 days at 180° F. The TEL peak was smaller at 3 days, as would be expected from the appearance of lead precipitation in the sample. The 3-day sample showed a large peak appearing at about 8 minutes and an increase in the broad peak observed 82 minutes. The 7-day sample saw the appearance of a small peak at 3.6 minutes and an increase of these materials eluted at 4 and 10 minutes and a dramatic decrease of TEL at 20 minutes, when compared to samples *A* and *B*. A large peak appeared at 15 minutes in the separation products of the 7-day sample. Because of the characteristics of the electron capture detector and a knowledge of the sample starting material, peaks could only have resulted from oxygenates, soluble lead alkyls, and/or degradation products of the halide scavengers present in the TEL mix. Since no evidence was found for disappearance of the halides or degradation from their original form as ethylene dibromide and ethylene dichloride, these halides were eliminated as possibilities in the identification of unknown species. This made oxygenates or soluble lead alkyls the most likely candidates.

It was hoped that by aging an unleaded blend otherwise identical in composition to that of Pb–168, differentiation between oxygenates and soluble lead products would be evident. Two chromatograms run under identical conditions are shown in figure D–2. The composition of both samples was identical, with the exception of the presence of 3 cm^3 gal^{-1} TEL in sample Pb–168. Sample 492 was 99.5 percent isooctane and 0.5 percent 1-ethylcyclopentene. These chromatograms show essentially the same patterns, with the exception of the large peaks at 3.5 minutes (ethylene dibromide) and 20.3 minutes

Table 7.—*Effect of extraction with diluted HNO_3 of SALS [1] on total lead determination by ESA [2]*

Sample	Storage time at 180° F, days	Total Pb, ppm		Difference, ppm	Pb removed, pct
		Before extraction	After extraction		
Pb–168	2	777	409	368	47.4
Pb–169	6	36,764	34,695	2,069	5.6

[1] Soluble alkyllead salts.

[2] Emission spectrographic analysis.

(TEL). This was evidence that none of the products separated and observed with the electron-capture detector was a soluble lead alkyl specie.

The final evidence used to define the general character of these reaction products is shown in the form of four chromatograms in figure D–3. The four samples represented in this drawing are those suspected of having contained the greatest amount of soluble lead alkyls, as indicated by differential lead analysis. These were Pb–168, after 2 days' aging at 180° F, and Pb–169, after 6 days' aging. Aliquots of both samples were extracted with dilute nitric acid to quantitatively remove all soluble lead alkyl salts. Differential lead analysis of these samples before and after extraction using the emission spectrograph is summarized in table 7. Nearly half the total lead was removed from Pb–168, and about 6 percent was removed from Pb–169. The removal of these materials should be seen in the chromatographic electron-capture response if the lead alkyls were of such a nature as to pass readily through the gas chromatographic separation column at the temperatures and carrier gas flow rates used in these procedures. Assuming that these materials possibly were of too-high molecular weight or too nonvolatile to pass through the column, it was decided to install a backflush valve in the chromatographic system, so that after the emergence of the TEL, the valve could be switched to elute any such materials off the front end of the separation column. Therefore, it is noted in figure D–3 that all four samples were backflushed at 21 or 22 minutes. The material flushed off the column after this point in time is seen as one large peak with evidence of individual compounds. Examination of the entire chromatogram for each sample shows little difference. The only possible major difference would have been in the size of the peak after backflushing.

For a better evaluation of this material, traps were made of the material eluted after backflush of 2-day Pb–168 before extraction. The material trapped was charged to a mass spectrometer for evaluation of the molecular weight of species collected. Only a trace of lead at mass 206, 207, and 208 was observed, and a slight trace of material at mass 224 was also seen. All other materials were of less than 200 molecular weight. The 206, 207, and 208 mass numbers correspond to the isotopes of lead, and the 224 mass would be the addition of oxygen to the 208 isotope. The amounts of these materials were extremely small. Other mass spectral analyses were made of materials eluted before the TEL with no evidence of lead, indicating that no soluble lead alkyls were responsible for these peaks. In light of these data, if would seem evident that the electron-capture response to materials separated in this chromatographic system is principally oxygenates, halides, and TEL. Little or no amount of soluble lead alkyls can be passed through the chromatographic column or eluted from the column by backflush. This latter fact indicates the transient and unstable nature of these intermediate reaction products.

Radiotracer Study of TEL Reactions

A radiotracer test of a leaded binary hydrocarbon blend containing cyclohexene-1-^{14}C was undertaken with the goal of (1) following the disappearance of TEL by GC analysis, (2) following the disappearance of cyclohexene both by direct GC analysis and by radioassay, and (3) measuring the distribution of radioactivity in reactants and products of reaction for the purpose of determining the role of cyclohexene in the lead precipitation process. After 5 days at 180° F, the radioactivity of the blend showed a 0.7-percent decline, and after 12 days, the total radioactivity loss was 2 percent. The blend was stored for a total of 29 days at the elevated temperature. Oxygen consumption was checked periodically by GC analysis, and when below 12 percent (from 21 percent), the blend was filtered and the precipitate was accumulated in a filter. Aliquots of the filtrate were analyzed by GC, and the radioactivity was checked by liquid scintillation radioassay, as described in section C of appendix A. The remaining filtrate was rebottled and stored at 180° F. Termination at 29 days was the consequence of reduced precipitation and oxygen consumption rates.

The sample obtained at the 5-day-storage interval contained five peaks not seen on the unstored material using a PE 900 analytical chromatograph with dual flame detector. These five species increased in size at 8-, 15-, and 29-day storage intervals. Also at 29 days, two additional peaks appeared. Attempts to identify any of these seven new peaks were unsuccessful. The filtrate from samples stored for 15 and 29 days was analyzed in the electron capture GC, but no unidentified peaks were observed.

Soluble and insoluble gum were measured after 29 days of storage. The lead precipitate that had been accumulated throughout the storage was dried and weighed. A summary of

Table 8.—*Summary of data from radiotracer experiment*

Storage time, days	Loss, pct				Gum,[1] mg/100 ml		Total Pb precipitate, mg/100 ml
	Radioactivity	Cyclohexene	TEL	O_2	Soluble	Insoluble	
5	0.76	15.4	47.4	48.6	--	--	23.8
8	2.3	16.0	78.9	39.5	--	--	43.9
15	4.6	43.1	92.1	45.7	--	--	56.2
29	7.1	42.9	99.1	19.5	6.1	20.4	56.2

[1] Gum determined only for 29-day sample.

the data obtained for this experiment is shown in table 8.

Attempts were made to determine radioactivity in soluble and insoluble gums and the lead precipitate to provide a radiotracer material balance. An apparent 7 percent of the radioactivity was unaccounted from previous determinations. Several solvents were investigated for these deposits, with nitric acid found best for the Pb ppt, and acetone for the gums. Counting efficiencies were low, and accuracy of these radioanalyses was considered below the routine sample. However, the total radioactivity found in these three materials amounted to 3.7 percent of the total in the original sample. Thus, perhaps half the loss was accounted for in these materials.

The data in table 8 were interpreted to indicate that cyclohexene was not incorporated into the lead precipitate during the early part of the storage, and perhaps not later, although nearly half of the cyclohexene changed its chemical state by the end of the 29 days of storage. Since more than 90 percent of the radioactivity originally present in the cyclohexene was still in solution at the end of the storage period, it appears that the loss in cyclohexene resulted from formation of oxidation products. Data presently available suggest that cyclohexene promotes lead precipitation, but reaction is not a simple combination of the two.

SUMMARY

The 110° F storage test was improved by changing storage containers to a size that provided a greater air-to-sample ratio and altering the procedure to include aeration at 4-week intervals. However, attempts to modify the ASTM D525 induction period bomb to improve correlations with storage stability were not successful, even though available oxygen during reaction time was increased and the amount of oxygen consumed was incorporated into a multiplying factor used in calculating predicted gum. It was concluded that electropolishing the interior of the metal bombs resulted ultimately in a changed surface that caused erratic results. Thereafter, glass beverage bottles were used in a similar technique, and good correlation was achieved with 110° F storage. Nomographs were developed to permit a rapid estimation of gum-forming potential of either leaded or unleaded gasolines, based upon the 16-hour oven test for predicting motor gasoline storage stability.

The extent to which certain sulfur compounds and hydrocarbons react to form gum during storage was investigated using a radiotracer technique. Blends were stored for about 2 months at 110° F. The thiols were the most reactive sulfur compounds. A differential-type analysis of gasolines before and after aging using gas chromatographic techniques was abandoned because of time requirements after showing that cycloolefins were particularly reactive in at least one gasoline that was analyzed. Efforts to use similar gas chromatographic equipment as a tool to measure gum in motor gasolines were not successful. A study of tetraethyllead reactions in binary hydrocarbon blends was conducted with the conclusion that the final structure of the lead precipitate is a function of the energy supplied to the reaction system. Precipitate formed at ambient or 110° F storage corresponds in elemental composition more nearly to diethylcarbonate, while the precipitate formed at 180° F is higher in molecular weight and the general structure is different. Soluble alkyllead compounds as intermediates to lead precipitation are too unstable and transient to isolate for identification by techniques used in this study. These compounds are probably triethyllead alkyls, but the diethyl-, monoethyl-, and inorganic lead compounds are less soluble and are the materials formed in hazing and deposition. A radiotracer study of tetraethyllead reaction with an olefin showed that the olefin was oxidized rapidly in the presence of TEL but did not incorporate into the lead precipitate. Less than 4 percent of the olefin could not be accounted in a material-balance study.

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APPENDIX A.—ANALYTICAL METHODS

In these studies, many analytical methods were investigated: some were discarded, some were modified and adopted, and some were developed and used for the specific purposes of this research. This appendix contains those techniques that became routine methods of analysis for the several phases of this investigation. Only the final routine is included here. Details of development are omitted or included in the body of this report. The following methods are discussed in this appendix:

A.—Storage Tests

1. 110° F Storage Test of Gasoline Stability
2. Analyzing Storage Samples
3. Method for Determining Oxygen in Outage of Test Bottles

B.—16-Hour Oven Test for Predicting Storage Stability

C.—Radiotracer Technique

A.—STORAGE TESTS

1. 110° F Storage Test of Gasoline Statibility

Cleaning the Storage Bottles

1. Scrub with a detergent solution and rinse with water.
2. Fill the bottle about half full with chromic acid cleaning solution, roll the bottle for complete contact of acid with the inner surface, pour out the acid, and allow the bottle to stand for at least 1 hour.
3. Rinse with tapwater, then invert and flush with a stream of distilled water.
4. Allow the bottle to drain. Dry overnight in a 300° F (150° C) oven.

Aging at 110° F

Filter the fuel through a membrane filter having 0.45-micron pore size to remove particles. Place 350 ml of fuel in each of twelve 40-oz (1, 180 ml), crown-and-cap, amber bottles. Seal with crimp-type caps lined with Teflon. Store in the dark at a constant temperature of 110° F. After each storage interval—8, 16, 32, and 52 weeks from the beginning of storage—remove two samples and analyze for gum. Use four samples as "floaters," for additional analysis at unscheduled times. Every 4 weeks during the storage, replenish the oxygen in the vapor space. To do this, remove all bottles, cool, aerate, and return to storage.

Aerating Storage Samples

1. Remove the sample from 110° F storage and cool to 32°–40° F.
2. Sweep the interior of the cooled bottle above the surface of the gasoline with a gentle stream of dried, compressed air for 2 minutes to insure that an adequate supply of air is in contact with the gasoline.
3. Recap the sample; when the sample has warmed to room temperature, return it to 110° F storage.

2. Analyzing Storage Samples

The fuel-insoluble gum and the precipitate are separated from the fuel by filtration. Soluble gum is determined on the filtered fuel as is "unwashed" gum by ASTM Method D381 (7). Insoluble gum is dissolved in organic solvents and weighed after evaporation of solvent. Precipitate is determined by weighing the filter.

Materials and Apparatus

Glass reservoir, with air-pressure connection and an approximately 9-mm-OD delivery tube.

Size 9 neoprene stopper, bored to accept delivery tube.

Gooch low-form filtering crucible: Pyrex, fritted disk, 30 ml, fine porosity.

Crucible holder.

Eight ASTM D381 air-jet gum beakers.

Two graduated bottles, at least 12 oz.

Stirring rod with policeman.

Gum solvent (1:1:1 acetone-benzene-methanol).

n-Heptane.

D381 gum bath; analytical balance; 200° F oven; covered container for beakers and filter.

Determining Soluble Gum

Weigh a filtering crucible (hereafter called "filter") and eight gum beakers. Assemble the reservoir-stopper-filter-holder arrangement for filtration, as shown in figure A–1. With gentle air pressure, pass the aged fuel from bottle A through the filter and collect the filtrate in a graduated bottle. Set aside. Pass the fuel from bottle B through the same filter, collecting in a separate bottle. Measure two portions of the filtrate from bottle A, each **equal to one-seventh** of the volume collected, into gum beakers. Do the same with filtrate from bottle B. Each of the four portions thus represents 50 ml of the original fuel. Determine air-jet gum on each by ASTM Method D381 (7). Average the results and report as soluble gum, in mg/100 ml.

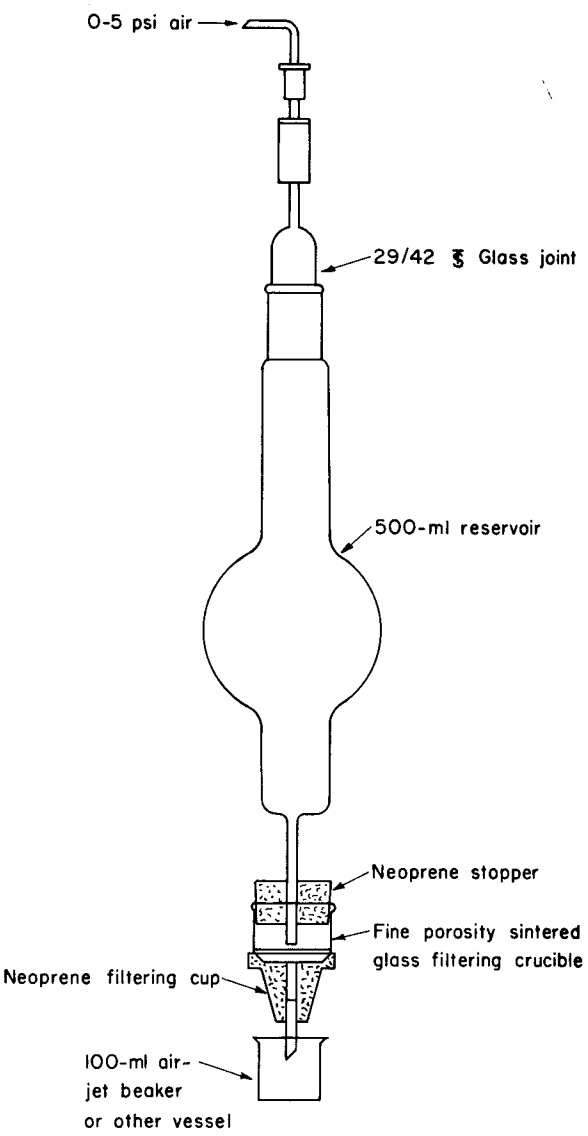


Figure A–1.—Filtering assembly.

Determining Insoluble Gum

Place a container beneath the filter. Rinse each bottle and the filter free of fuel by adding three successive 50-ml portions of heptane into each bottle by gently swirling, and pass rinsings through filter. Discard rinsings.

Place a weighed gum beaker beneath the filter. Rinse and police bottle A with 15 ml of gum solvent, then pass the solution through filter into beaker. Repeat twice with 15- to 20-ml portions of solvent for a total of not more than 50 ml of solution in gum beaker.

Place another gum beaker beneath filter and carry out the gum solvent steps on bottle B.

Evaporate solvent from the two solutions by the air-jet method described in ASTM D381 and weigh the residues.

$$\text{Insoluble gum, mg/100 ml} = \frac{\text{residue A, mg} + \text{residue B, mg}}{7}$$

To obtain Total Gum, add the insoluble gum and soluble gum values.

Determining Precipitate

To determine the precipitate collected on the filter, dry the filter in a 200° F oven for 1 hour, cool at least 2 hours, and weigh.

$$\text{Precipitate, mg/100 ml} = \frac{\text{precipitate, mg}}{7}$$

3. Method for Determining Oxygen in Outage of Test Bottles

A sample of the vapor (outage) is withdrawn from the closed bottle through a septum and injected into a gas chromatograph. This yields an oxygen-argon peak and a nitrogen peak from the air in the outage. Oxygen content is calculated from the ratio of the peak heights for oxygen and nitrogen from the outage compared with the ratio of those from air.

Materials and Apparatus

Gas chromatograph equipped with thermistor detector; 5-ft by ¼-in copper column; 30- to 60-mesh molecular sieve 13X, conditioned at 400° to 600° F for 6 hours with helium; ambient temperature; 67-ml/min helium flow; 25-ma filament current.

Procedure

Inject an amount of the sample of outage to produce a nearly full-scale nitrogen peak (50 to 80 μl). Repeat once or twice to get a duplicate pattern. Inject an amount of air to give a nitrogen peak of about the same height, and repeat for a duplicate.

Calculations

Since the chromatographic column does not separate oxygen and argon, the oxygen peak must be corrected for the latter. This is a simple matter, after known quantities of argon have been injected and the sensitivity of the detector to this gas has been established.

Comparison of peak heights is used in the calculations for oxygen because of the presence of hydrocarbon vapors in the outage. Calculate oxygen by the following steps:

1. Correct the average oxygen peak height for argon in the air sample.
2. Divide this corrected peak height by the average height of the nitrogen peak. Quotient is R_a.
3. In like manner, figure the oxygen/nitrogen ratio, R_s, for the replicate injections of outage sample.
4. The volume percent of oxygen in air is 1/3.71748 that of nitrogen. Assuming that the ratio of oxygen to nitrogen is constant unless the oxygen is depleted, calculate oxygen by the following formula:

$$\frac{1}{1+3.71748\left(\frac{R_a}{R_s}\right)} \times 100 = \text{oxygen in air in bottle outage on argon-free basis, pct.}$$

Convert the result to a "whole air" basis by multiplying by 0.99.

B.—16-HOUR OVEN TEST FOR PREDICTING STORAGE STABILITY

1. Method of Cleaning Beverage Bottles

1. Scrub with a detergent solution, and rinse with water.
2. Add chromic acid cleaning solution to the bottle, swirl, and roll the bottle to insure complete contact of acid with entire inner surface.
3. Rinse with tap water, then invert the bottle and flush with a stream of distilled water.
4. Allow the bottle to drain. Dry overnight in a 300° F (150° C) oven.

2. Aging at 200° F

Filter the fuel through a GA–6 Metricel, 0.45-micron pore-size filter to remove particles. Place

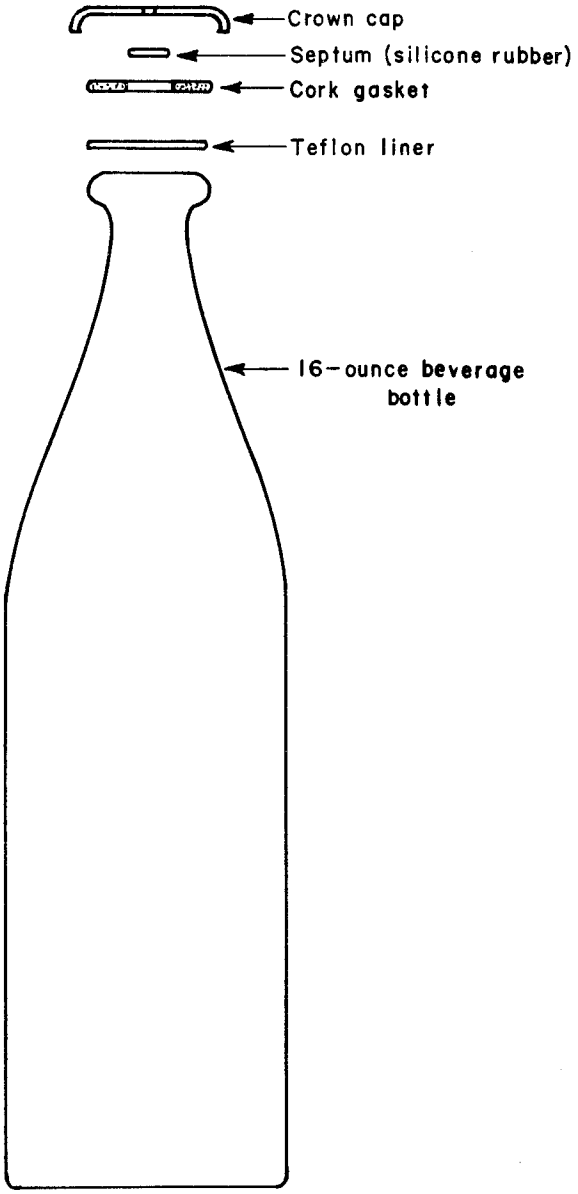


Figure A–2.—Beverage Bottle and Cap.

130 ml of fuel in each of two 16-oz beverage bottles at room temperature (fig. A–2). Seal the bottles with special crimp-type caps lined with Teflon. These caps are designed to permit puncture and withdrawal of vapor samples from the outage with a hypodermic syringe. For this purpose, each cap is fitted with a septum in the center. Weigh each bottle and contents to nearest 0.1 g. Place each within a steel jacket (fig. A–3),

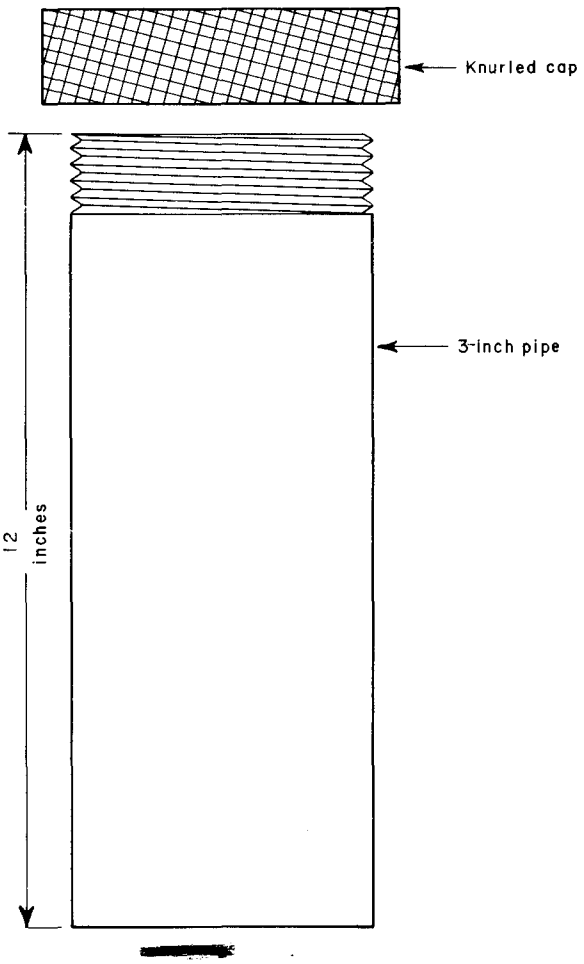


Figure A–3.—Metal Safety Shield for Beverage Bottle Oven Test.

close, and heat the jackets and contents for 16 hours in a 200° F oven. Cool the assembly and then the bottles themselves in a water bath and weigh the dry bottle to check for loss. Determine the oxygen in the outage of each by gas chromatography. Open the bottles and analyze the aged fuel for gums and residue.

3. Analyzing Aged Fuel

The fuel-insoluble gum and inorganic residue are separated from the fuel by filtration. Soluble gum is determined on the filtered fuel by ASTM Method D381. Insoluble gum is dissolved in gum solvent and measured by evaporation of solvent. Inorganic residue is determined by weighing the filter.

Materials and Apparatus

Glass reservoir, with air-pressure connection and an approximately 9-mm-OD delivery tube. Size 9 neoprene stopper, bored to accept delivery tube.

Gooch low-form filtering crucible: Pyrex, fritted disk, 30 ml, fine porosity.

Crucible holder.

Eight ASTM D381 air-jet gum beakers.

Stirring rod with policeman.

Gum solvent (1:1:1 acetone-benzene-methanol).

n-Heptane.

D381 gum bath; analytical balance; 200° F oven; desiccator without desiccant.

Determining Soluble Gum

Weigh a filtering crucible (hereafter called "filter") and eight gum beakers. Assemble the reservoir-stopper-filter-holder arrangement for filtration. With gentle air pressure, pass the aged fuel from bottle A through the filter and collect the filtrate. Set aside. Pass the fuel from bottle B through the same filter, collecting in a separate container. Make duplicate determinations of air-jet gum in each filtrate. Report their average as soluble gum, mg/100 ml.

Determining Insoluble Gum

Place a container beneath the filter. Rinse each bottle and the filter free from fuel by adding three successive 50-ml portions of heptane into each bottle by gently swirling, and pass rinsings through filter. Discard rinsings.

Place a weighed gum beaker beneath filter. Rinse and police bottle A with 15 ml of gum solvent, then pass the solution through filter into beaker. Repeat twice with 15- to 20-ml portions of solvent for a total of not more than 50 ml of solution in gum beaker.

Place another gum beaker beneath filter and carry out the gum solvent steps on bottle B.

Run gum method on the two solutions.

$$\text{Insoluble gum, mg/100 ml} = \frac{\text{residue A, mg} + \text{residue B, mg}}{2.6}$$

Determining Inorganic Residue

To determine the residue collected on the filter, dry the filter in a 200° F oven for 1 hour, cool at least 2 hours, and weigh.

$$\text{Inorganic residue, mg/100 ml} = \frac{\text{residue, mg}}{2.6}$$

To obtain total gum, add the insoluble gum to the soluble gum value.

C.—RADIOTRACER TECHNIQUES

During studies of the relative contributions of various compounds in gum formation, the

extent to which a compound reacted was determined by radiotracer techniques. Compounds labeled either with ^{3}H (tritium), ^{14}C, or ^{35}S served as tracers. In the method, the sample—a gasoline or special blend of compounds of interest—was tagged by the addition of a small amount of one or two of the labeled compounds and aged by means of storage at 110° F; the gum was recovered and the radioactivity of the sample and products were determined by liquid scintillation counting. This is a sensitive and convenient way to measure small amounts of radioactivity in liquid samples. Activity data on the gum, the unreacted sample, and the original fuel or blend permitted calculation of both the amount of the test compound reacting to form gum and a material balance on the tracer.

1. Materials and Apparatus

Tri-Carb liquid scintillation spectrometer, model 314EX, Packard Instrument Co.

Screw cap vials, 22 ml, either low-potassium glass or polyethylene.

Fluor scintillation solution—5 g "PPO" (2,5-diphenyloxazone) and 0.1 g "POPOP" [1,4-bis-2-(5-phenyloxazolyl)-benzene] dissolved in 1 liter of reagent-grade toluene.

Toluene-^{3}H, solutions of known tritium activity used as internal standard, from 2.2 to 10 $\times$ 10^{6} dpm/ml activity.

Toluene-^{14}C, solutions of known ^{14}C activity used as internal standard for measurements of both ^{14}C and ^{35}S, from 0.4 to 3.6 $\times$ 10^{6} dpm/ml (disintegrations per minute per ml) activity.

Toluene-^{3}H and toluene-^{14}C solutions of standard radioactivity, one of each, sealed in glass ampoules, Packard Instrument Co.; used for daily check of spectrometer operation.

2. Procedure

A modification of the method of Whisman [1] proved suitable for the fuel stability study. No internal cleaning of the vials holding the solutions to be counted (counting vials) was employed; however, because of collection of dust and paper particles, the outside of each plastic vial was cleaned by blowing with air and wiping with a tissue. Each "counting solution" consisted of the sample solution in 15 ml of fluor in a counting vial. Solutions prepared as standards contained internal standard, in addition. Aliquots of sample and of internal standard were chosen to yield count rates of 5,000 and 50,000 counts per minute, respectively, or a 1-to-10 activity ratio of sample to standard.

The sample of liquid or gum was dissolved in 25 ml of fluor. A preliminary count was made on a portion of the sample solution—500 microliters of the dissolved gum solution or 25 to 100 microliters for liquids—in the fluor to learn the correct aliquot for the desired activity. The predetermined aliquot of sample then was added to each of two vials of fluor and, to one of these was added the proper amount of internal standard having the same isotope as the sample. These, together with a vial of fluor only for a 30-minute background count, were placed in the cold chest of the instrument and counted after an hour of cooling. A practice of counting each tagged solution to 100,000 counts reduced the counting error resulting from the random nature of radioactive decay to an acceptable level ($\pm$ 1 percent). When the test sample contained two isotopes, three vials of fluor were used: sample only, sample plus tritium, and sample plus carbon-14. The Packard instrument automatically printed out time and count of each sample, then changed sample and continued. The printout was used to prepare a Flexowriter data tape for computation of the activities present. The following counting efficiencies, expressed in percentages, were attained:

Tracer	Gums	Gasolines and blends
^{3}H	3 to 10	14
^{14}C	46 to 57	58
^{35}S	43	58

[1] Whisman, M. L., B. H. Eccleston, and F. E. Armstrong. Liquid Scintillation Counting of Tritiated Organic Compounds. Anal. Chem., v. 32, No. 4, 1960, pp. 484–486.

APPENDIX B.—FUELS AND SAMPLES

Two sets of fuels were used for the major part of the studies included in this report. The first set of 12 gasolines, tabulated in table B–3, included both full-boiling-range gasolines and blending stocks. These samples did not contain additives and were used in the initial investigations of motor gasoline storage stability. Inspection tests for the initial properties of these samples are shown in the table. Final development of the 16-hour oven test for predicting storage stability was based upon the 24 fuels shown in tables B–1 and B–2. These fuels all contain TEL and other additives. The antioxidant and metal deactivator content of the last 11 fuels tabulated in table B–2 are detailed in table B–1.

Table B–1.—*Compositions of fuel 14–24*

Gasoline	Blend stocks	Additives[1]
14	70 pct reformate 30 pct light, straight run	PDA, 5 lb/1,000 bbl MDA, 1 lb/1,000 bbl Tetralkyllead
15	22 pct light catalytic crack 20 pct light alkylate 58 pct light catalytic crack	Do.
16	40 pct low-boiling, straight run 48 pct tops (aromatic C_6, C_7, C_8) 12 pct bottoms (C_9+)	Do.
17	30 pct low-boiling, straight run 30 pct light catalytic crack 20 pct light alkylate 20 pct high-boiling, straight run	Do.
18	Same as fuel 17	Do.
19	No. 17 plus 1 pct thermally cracked stock A	None.
20	No. 18 plus 1 pct thermally cracked stock A	Do.
21	No. 17 plus 3 pct thermally cracked stock A	Do.
22	No. 18 plus 3 pct thermally cracked stock A	Do.
23	No. 17 plus 1 pct thermally cracked stock B	Do.
24	No. 17 plus 3 pct thermally cracked stock B	Do.

[1] PDA = N, N'–di–*sec*–butyl–*p*–phenylenediamine.
MDA = N, N'–disalicylidene–1,2–diaminopropane.

Table B–2.—*Initial properties of gasolines*

	Fuel 1 (commercial)	Fuel 2 (commercial)	Fuel 3 (military)	Fuel 4 (commercial)	Fuel 5 (military)	Fuel 6 (commercial)	Fuel 7 (military)	Fuel 8 (military)	Fuel 9 (military)	Fuel 10 (military)	Fuel 11 (military)	Fuel 12 (commercial)
Gravity, °API	62.4	59.7	58.7	67.8	62.9	60.0	55.9	55.9	58.2	57.9	57.9	64.8
Boiling point, °F:												
Initial boiling point	93	88	98	98	100	82	100	112	102	98	102	84
10 pct recovered	119	128	140	121	148	114	146	146	142	144	144	122
50 pct recovered	203	240	224	179	218	224	214	212	216	220	222	206
90 pct recovered	338	372	328	319	302	356	352	348	314	328	332	326
End point	423	480	404	414	362	402	406	402	378	402	410	390
Sulfur, wt pct	.06	0.021	0.017	0.031	0.020	0.012	0.041	0.039	0.016	0.019	0.019	0.027
Fluorescent indicator adsorption, vol pct:												
Saturates	72.5	60.0	63.0	69.5	80.0	58.0	62.0	63.0	62.5	63.5	63.0	66.0
Olefins	8.5	18.5	10.5	15.0	7.0	12.0	8.5	8.0	10.0	8.5	9.5	12.0
Aromatics	19.0	21.5	26.5	15.5	13.0	30.0	29.5	29.0	27.5	28.0	27.5	22.0
Induction period, min	1440	483	720	679	---	754	---	---	---	---	---	332
Lead, g/gal	2.29	1.31	2.76	1.31	2.75	1.40	2.77	2.20	2.74	3.03	3.99	2.02

	Fuel 13 (military)	Fuel 14 (reformate)	Fuel 15 (high olefin)	Fuel 16 (high aromatic, low olefin)	Fuel 17 (high paraffin)	Fuel 18 (#17+TEL)	Fuel 19 (#17+1 pct A)[1]	Fuel 20 (#19+TEL)	Fuel 21 (#17+3 pct A)[1]	Fuel 22 (#21+TEL)	Fuel 23 (#17+1 pct B)[2]	Fuel 24 (#17+3 pct B)[2]
Gravity, °API	52.3	54.6	60.9	53.8	64.2	63.5	64.2	64.0	63.8	64.0	63.7	63.5
Boiling point, °F:												
Initial boiling point	96	96	99	98	100	100	---	---	---	---	---	---
10 pct recovered	148	146	135	151	142	139	---	---	---	---	---	---
50 pct recovered	234	226	204	216	203	195	---	---	---	---	---	---
90 pct recovered	324	328	302	296	298	298	---	---	---	---	---	---
End point	406	---	---	---	---	---	---	---	---	---	---	---
Sulfur, wt pct	0.006	0.010	0.015	0.010	0.012	0.010	---	---	---	---	---	---
Fluorescent indicator adsorption, vol pct:												
Saturates	59.0	65.0	60.0	68.0	82.0	80.5	80.5	81.0	80.0	80.5	80.5	78.0
Olefins	0.0	1.5	18.5	.5	5.0	6.5	6.0	6.0	5.5	6.5	5.5	7.5
Aromatics	41.0	33.5	21.5	31.5	13.0	13.0	13.5	13.0	14.5	13.0	14.0	14.5
Induction period, min	>5040	480+	480+	480+	480+	480+	480+	480+	480+	480+	480+	480+
Lead, g/gal	1.54	2.95	3.10	2.64	2.58	3.87	2.57	3.79	2.56	3.70	2.77	2.43

[1] Thermally cracked stock A.
[2] Thermally cracked stock B.

Table B–3.—*Inspection tests of samples*

	BOG–185 (regular gasoline)	BOG–186 (premium gasoline)	BOG–187 (cat poly stock)	BOG–190 (reformate)	BOG–191 (cat poly stock	BOG–193 (cat cracked stock)	BOG–194 (alkylate)	BOG–195 ("ABC" stock)	BOG–196 (T.C. stock)	BOG–198 (90 pct 185, 10 pct 187)	BOG–199 (90 pct 186, 10 pct 187)	BOG–202 (regular gasoline)
Specific gravity	0.7461	0.7012	0.7140	0.7914	0.7365	0.7550	0.6971	0.8560	0.7398	0.7452	0.7029	0.7581
Gravity ° API	58.2	70.4	67.8	47.4	60.8	55.9	71.5	33.8	59.7	---	---	55.2
D–86 Boiling point, ° F:												
Initial boiling point	106	102	80	98	124	108	108	222	110	---	---	90
10 pct recovered	140	124	144	160	252	142	150	228	152	---	---	134
50 pct recovered	238	196	250	262	286	240	224	232	258	---	---	234
90 pct recovered	344	338	412	332	324	380	304	252	358	---	---	362
End point	422	422	414	410	358	430	404	388	404	---	---	242
Fluorescent indicator adsorption, pct:												
Saturates	62.6	80.6	5.4	44.5	5.7	36.4	100.0	8.7	58.6	---	---	48.8
Olefins	15.4	13.3	74.5	2.6	94.3	44.7	0	0	31.7	---	---	18.8
Aromatics	22.0	6.1	20.1	52.9	0	18.9	0	91.3	9.7	---	---	32.4
D–875 Analysis, pct:												
Saturates	72.5	79.0	7.0	41.0	9.0	38.0	99.0	9.0	59.0	---	---	47.0
Olefins	16.2	14.2	81.5	2.3	91.0	51.5	0	0	37.9	---	---	22.5
Aromatics	10.9	6.8	11.5	56.7	0	10.5	1.0	91.0	3.1	---	---	30.5
Gum, mg/100 ml:												
Air-jet	1.5	1.1	2.6	0.6	0.2	1.0	0	1.0	1.7	---	---	1.8
Vacuum transfer	21.7	14.4	60.7	47.9	4.9	15.0	35.2	24.0	45.0	---	---	37.2
Copper dish	21.6	15.8	17.2	27.4	42.3	155.9	0	7.9	403.0	---	---	19.7
Sulfur lamp pct	.0264	.0195	.0029	.0029	.0198	.0643	.0005	.0010	.0439	---	---	.0225
Thiols do	.00008	.00024	---	---	.00042	.00112	---	---	.00585	---	---	.00003
Light transmission [1] do	79.6	89.6	74.1	88.6	88.7	92.1	93.2	100	92.6	---	---	90.5

[1] Lumetron.

APPENDIX C.—DATA AND CORRELATIONS OBTAINED DURING THE DEVELOPMENT OF A RAPID STABILITY-PREDICTION METHOD

To avoid cluttering the text with data that are essential to support the statements and conclusions offered in the body of this report, much of this material is presented in this appendix. Both the tables and figures are included in the order of their reference in the text. Tables C–1 through C–6 show the development steps and correlations that were made between data obtained using a modified ASTM induction bomb test for stability and data obtained from 110° F storage on a series of fuels that are discussed in appendix B. Table C–7 lists tabular data obtained from the final test procedure that was developed using a 16-hour oven test and beverage bottles as storage containers. These data and the statistical analyses shown in table C–8 and C–9 conclude the efforts and successful development of the storage stability prediction test.

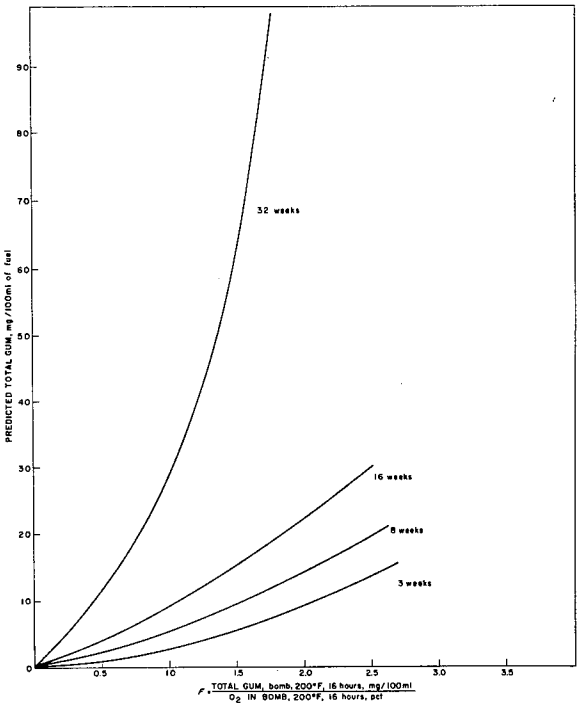


Figure C–1.—Total gum correlation, neat gasolines, 110° F storage.

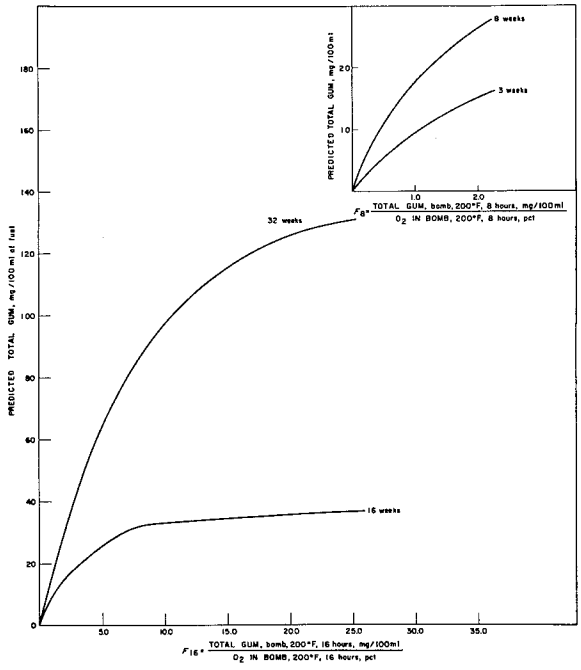


Figure C–2.—Total gum correlation, leaded gasolines, 110° F storage.

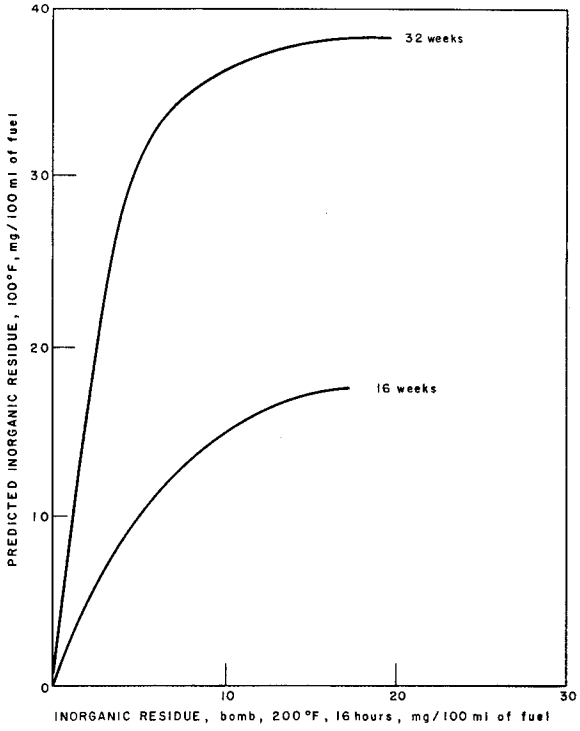


Figure C–3.—Inorganic residue, leaded gasolines, 110° F storage.

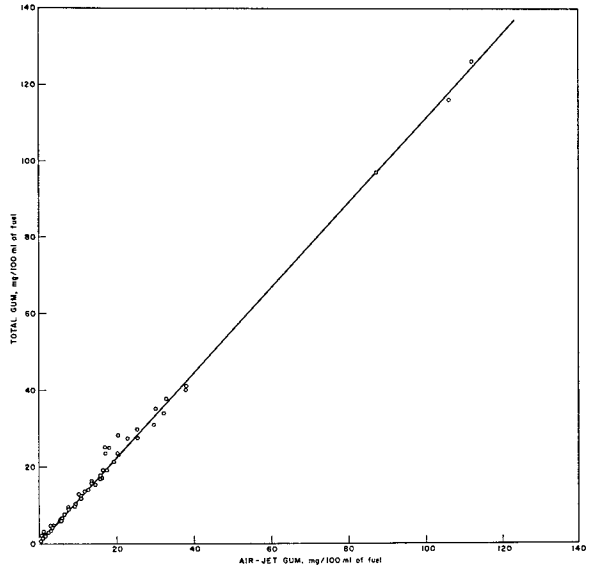


Figure C–4.—Ratio of total gum to air-jet gum.

Table C–1.—*Data from rapid stability tests of additive fuels at 200° F, mg/100 ml of fuel*

Fuel	Additive			Initial		8-hour test					16-hour test				
	TEL[1]	Diamine[2]	Phenol[3]	Total gum	O_2 in outage, pct	Inorganic residue	Fuel-insoluble gum	Soluble gum	Total gum	O_2 in outage, pct	Inorganic residue	Fuel-insoluble gum	Soluble gum	Total gum	O_2 in outage, pct
BOG–185				1.9	21	--	1.5	5.7	7.2	19	--	2.9	9.9	12.8	11
BOG–186				1.1	21	--	1.2	3.1	4.3	19	--	--	--	4.2	18
BOG–202				1.4	21	--	.8	2.7	3.5	20	--	1.7	11.7	13.4	7
BOG–295				0	21	--	.5	3.8	4.3	21	--	.2	.9	1.1	21
BOG–185	X			2.4	21	0	1.5	11.0	12.5	16	10.3	2.0	16.0	18.0	9
BOG–186	X			1.1	21	0	1.6	9.3	10.9	18	5.8	5.2	11.7	16.9	10
BOG–202	X			3.2	21	1.3	2.3	13.2	15.5	10	4.3	1.9	16.2	18.1	1
BOG–295	X			1.0	21	3.1	3.2	2.1	5.3	20	12.9	2.4	4.7	7.1	0
BOG–185	X	X		2.0	21	0	1.0	9.5	10.5	17	3.4	3.6	30.3	33.9	4
BOG–186	X	X		1.3	21	2.2	1.1	8.9	10.0	19	1.4	3.2	13.0	16.2	10
BOG–202	X	X		1.7	21	0	2.9	11.7	14.6	15	4.2	1.2	19.7	20.9	0
BOG–295	X	X		.2	21	0	1.4	1.4	2.8	20	.1	1.6	3.6	5.2	19
BOG–185	X		X	1.6	21	0	1.0	4.4	5.2	17	8.8	2.2	16.2	18.4	9
BOG–186	X		X	1.2	21	0	2.9	3.0	5.9	21	3.8	1.8	9.8	11.6	12
BOG–202	X		X	2.5	21	0	2.4	11.5	13.9	19	5.2	1.5	17.7	19.2	0
BOG–295	X		X	.3	21	0	3.8	1.1	4.9	20	0	.9	1.1	2.0	19
BOG–185		X		2.1	21	0	1.6	10.3	11.9	21	0	2.5	8.0	10.5	21
BOG–186		X		1.4	21	0	3.0	2.9	5.9	20	0	1.7	3.4	5.1	20
BOG–202		X		2.1	21	0	1.9	8.4	10.3	15	0	.8	8.7	9.5	18
BOG–295		X		.9	21	0	2.2	1.7	3.9	17	0	1.0	.6	1.6	20
BOG–185			X	2.3	21	0	1.3	4.1	5.4	21	2.2	3.0	15.2	18.2	20
BOG–186			X	1.5	21	0	1.6	3.3	4.9	20	0	1.8	3.8	5.6	19
BOG–202			X	1.9	21	0	1.1	4.0	5.1	20	0	1.1	8.9	10.0	17
BOG–295			X	.8	21	0	2.7	1.5	4.2	19	0	.3	.7	1.0	19

[1] Uninhibited tetraethyllead motor mix, 3 ml/gal of fuel.
[2] N,N–di–*sec*–butyl–*p*–phenylenediamine, 10 lb/1,000 bbl of fuel.
[3] 2,6–Di–*tert*–butyl–4–methylphenol, 10 lb/1,000 bbl of fuel.

Table C–2.—*Data from 110° F storage tests of additive fuels, mg/100 ml of fuel*

FUEL	Additive			Initial		3-week test				8-week test					16-week test					32-week test				
	TEL	Diamine	Phenol	Total gum	O_2 in outage, pct	Inorganic residue	Fuel-insoluble gum	Soluble gum	Total gum	O_2 in outage, pct	Inorganic residue	Fuel-insoluble gum	Soluble gum	Total gum	O_2 in outage, pct	Inorganic residue	Fuel-insoluble gum	Soluble gum	Total gum	O_2 in outage, pct	Inorganic residue	Fuel-insoluble gum	Soluble gum	Total gum	O_2 in outage, pct
BOG–185				1.9	21	--	0.4	3.7	4.1	20	--	0.8	5.6	6.4	19	--	1.9	11.8	13.7	19	--	5.2	32.6	37.8	13
BOG–186				1.1	21	--	.4	1.8	2.2	21	--	.3	1.1	1.4	20	--	.6	1.8	2.4	20	--	2.3	3.6	5.9	20
BOG–202				1.4	21	--	.5	6.0	6.5	19	--	.5	6.0	6.5	16	--	1.0	15.7	16.7	13	--	3.7	102	106	7
BOG–295				0	21	--	.2	.4	.6	21	--	--	--	--	--	--	.8	.8	1.6	20	--	.8	1.1	1.9	20
BOG–185	X			2.4	21	0	.6	9.0	9.6	16	0.2	2.5	16.4	18.9	18	1.6	3.4	20.1	23.5	18	32.2	2.3	25.3	27.6	20
BOG–186	X			1.1	21	.1	.4	5.4	5.8	18	0	1.7	10.3	12.0	16	5.2	2.5	13.4	15.9	16	24.2	6.6	16.9	23.5	20
BOG–202	X			3.2	21	0	.9	10.7	11.6	14	3.9	1.5	17.4	18.9	12	10.8	2.1	37.9	40.0	0	29.0	13.7	111.6	125	4
BOG–295	X			1.0	21	0	.5	1.5	2.0	19	0	.9	.2	1.1	21	13.2	1.3	4.2	5.5	5	21.7	42.1	44.2	86.3	0
BOG–185	X	X		2.0	21	0	.4	2.5	2.9	19	.1	1.3	6.2	7.5	18	4.8	5.8	20.2	26.0	14	41.3	3.6	25.2	28.8	20
BOG–186	X	X		1.3	21	0	.3	1.9	2.2	19	0	.7	2.9	3.6	19	.3	1.3	3.9	5.2	16	21.0	6.9	18.0	24.9	20
BOG–202	X	X		2.0	21	0	.8	9.3	10.1	15	3.2	.8	16.3	17.1	18	9.1	1.2	29.6	30.8	0	26.7	9.8	87.2	97.0	8
BOG–295	X	X		.2	21	0	.4	1.1	1.5	19	0	.9	.6	1.5	21	0	1.0	.8	1.8	16	0	1.3	.8	2.1	21
BOG–185	X		X	1.6	21	0	.5	2.6	3.1	20	0	.9	14.6	15.5	19	14.1	2.2	19.2	21.4	16	34.1	4.6	22.7	27.3	20
BOG–186	X		X	1.1	21	0	.3	1.7	2.0	20	0	1.1	7.6	8.7	18	7.1	2.4	10.3	12.7	17	27.5	7.6	17.2	24.8	21
BOG–202	X		X	2.5	21	0	.7	8.9	9.6	15	3.2	1.1	15.9	17.0	17	10.1	1.8	32.2	34.0	0	35.6	10.0	106	116	5
BOG–295	X		X	.3	21	0	.4	1.2	1.6	21	0	1.0	1.2	2.2	21	0	.8	.6	1.4	19	0	1.2	.4	1.6	21
BOG–185		X		2.1	21	0	.5	1.0	1.5	20	0	1.0	3.2	4.2	21	.3	1.2	4.4	5.6	21	0	1.7	5.8	7.5	21
BOG–186		X		1.4	21	0	.4	1.3	1.7	18	0	1.0	2.3	3.3	21	.2	1.1	2.2	3.3	21	0	1.7	3.7	5.4	21
BOG–202		X		2.1	21	0	.4	2.8	3.2	20	0	.4	3.9	4.3	21	.1	1.0	3.9	4.9	21	0	1.6	10.9	12.5	20
BOG–295		X		.9	21	0	.4	.7	1.1	19	0	.9	1.2	2.1	21	.2	.9	.9	1.8	20	0	1.2	0	1.2	21
BOG–185			X	2.3	21	0	.4	3.1	3.5	20	0	1.2	5.7	6.9	19	4.3	1.4	12.6	14.0	18	13.0	4.8	30.3	35.1	16
BOG–186			X	1.5	21	0	.3	2.6	2.9	19	0	1.1	2.1	3.2	21	.1	.8	2.7	3.5	21	0	1.8	2.9	4.7	21
BOG–202			X	1.9	21	0	.5	5.1	5.6	20	0	.4	4.9	5.3	19	0	1.2	7.6	8.8	19	0	2.9	38.1	41.0	0
BOG–295			X	.8	21	0	.5	1.8	2.3	21	0	.9	.9	1.8	18	0	.9	0	.9	21	0	1.3	.2	1.5	21

Table C–3.—*Gum correlation for neat fuels*

Fuel	Description	F[1]	Total gum in 110° F storage											
			3 weeks			8 weeks			16 weeks			32 weeks		
			D[2]	P[3]	Dev[4]	D[2]	P[3]	Dev[4]	D[2]	P[3]	Dev[4]	D[2]	P[3]	Dev[4]
BOG–185	Regular gasoline	1.16	4.1	3.6	0.5	6.4	6.6	0.2	13.7	11.1	2.6	37.8	36.6	1.2
BOG–186	Premium gasoline	.23	2.2	.4	1.8	1.4	1.0	.4	2.4	1.9	.5	5.9	5.0	.9
BOG–202	Regular gasoline	1.91	6.5	8.4	1.9	6.5	13.3	6.8	16.7	20.9	4.2	106	124	18
BOG–295	Alkylate blending stock	.05	.6	.2	.4	--	.4	--	1.6	.5	1.1	1.9	.8	1.1
BOG–193	Cat-cracked blending stock	1.05	2.1	3.0	.9	6.3	5.7	.6	6.4	9.8	3.4	25.7	31.0	5.3
BOG–194	Alkylate blending stock	.08	0	.2	.2	.3	.5	.2	.2	.6	.4	.7	1.0	.3
BOG–195	AvGas blending stock	.53	3.3	1.0	2.3	1.3	2.5	1.2	3.1	4.4	1.3	7.7	12.3	4.6

[1] F = mg total gum, 16 hr at 200° F / pct O_2, 16 hr at 200° F

[2] Determined, mg/100 ml.
[3] Predicted, mg/100 ml.
[4] Deviation, mg/100 ml.

Table C–4.—*Gum correlation for fuels with antioxidants*

Sample	F[1]	Total gum in 110° F storage											
		3 weeks			8 weeks			16 weeks			32 weeks		
		D[2]	P[3]	Dev[4]	D[2]	P[3]	Dev[4]	D[2]	P[3]	Dev[4]	D[2]	P[3]	Dev[4]
BOG–185 + DA[5]	0.50	1.5	0.9	0.6	4.2	2.4	1.8	5.6	4.1	1.5	7.5	11.4	3.9
BOG–186 + DA[5]	.26	1.7	.4	1.3	3.3	1.2	2.1	3.3	2.1	1.2	5.4	5.6	.2
BOG–202 + DA[5]	.53	3.2	1.0	2.2	4.3	2.5	1.8	4.9	4.4	.5	12.5	12.3	.2
BOG–295 + DA[5]	.08	1.1	.2	.9	2.1	.5	1.6	1.8	.6	1.2	1.2	1.0	.2
BOG–185 + PA[6]	.91	3.5	2.3	1.2	6.9	4.8	2.1	14.0	8.2	5.8	35.1	24.8	10.3
BOG–186 + PA[6]	.29	2.9	.5	2.4	3.2	1.4	1.8	3.5	2.4	1.1	4.7	6.3	1.6
BOG–202 + PA[6]	.59	5.6	1.2	4.4	5.3	2.8	2.5	8.8	5.0	3.8	41.0	14.0	27.0
BOG–295 + PA[6]	.05	2.3	.2	2.1	1.8	.4	1.4	.9	.5	.4	1.5	.8	.7

[1] F = mg total gum, 16 hr at 200° F / pct O_2, 16 hr at 200° F
[2] Determined, mg/100 ml.
[3] Predicted, mg/100 ml.
[4] Deviation, mg/100 ml.
[5] Diamine antioxidant.
[6] Phenol antioxidant.

Table C–5.—*Gum correlation for leaded fuels*

Sample	F_8[1]	F_{16}[2]	Total gum in 110° F storage											
			3 weeks			8 weeks			16 weeks			32 weeks		
			D[3]	P[4]	Dev[5]	D[3]	P[4]	Dev[5]	D[3]	P[4]	Dev[5]	D[3]	P[4]	Dev[5]
BOG–185 + TEL	0.78	2.0	9.6	7.9	1.7	18.9	15.1	3.8	23.5	16.0	7.5	27.6	30.0	2.4
BOG–186 + TEL	.60	1.7	5.8	6.3	.5	12.0	12.5	.5	15.9	14.0	1.9	23.5	26.0	2.5
BOG–202 + TEL	1.55	18.1	11.6	12.9	1.3	18.9	23.0	4.1	40.0	34.5	5.5	125	122	3
BOG–295 + TEL	.26	7.1	2.0	3.0	1.0	1.1	6.8	5.7	5.5	30.4	24.9	86.3	80.2	6.1
BOG–185 + TEL + DA[6]	.62	8.5	2.9	6.4	3.5	7.5	12.8	5.3	26.0	32.3	6.3	28.8	89.0	60.2
BOG–186 + TEL + DA[6]	.53	1.6	2.2	5.7	3.5	3.6	11.5	7.9	5.2	13.0	7.8	24.9	24.2	.7
BOG–202 + TEL + DA[6]	.97	20.9	10.1	9.3	.8	17.1	17.4	.3	30.8	34.0	4.2	97.0	127	30
BOG–295 + TEL + DA[6]	.14	.3	1.5	1.7	.2	1.5	4.0	2.5	1.8	3.0	1.2	2.1	5.6	3.5
BOG–185 + TEL + PA[7]	.31	2.0	3.1	3.6	.5	15.5	7.8	7.7	21.4	16.0	5.4	27.3	30.0	2.7
BOG–186 + TEL + PA[7]	.28	1.0	2.0	3.3	1.3	8.7	7.2	1.5	12.7	9.0	3.7	24.8	16.0	8.8
BOG–202 + TEL + PA[7]	.73	19.2	9.6	7.5	2.1	17.0	14.4	2.6	34.0	35.0	1.0	116	124	8
BOG–295 + TEL + PA[7]	.25	.1	1.6	3.0	1.4	2.2	6.5	4.3	1.4	1.6	.2	1.6	2.5	.9

[1] F_8 = mg total gum, 8 hr at 200° F / pct O_2, 8 hr at 200° F
[2] F_{16} = mg total gum, 16 hr at 200° F / pct O_2, 16 hr at 200° F
[3] Determined, mg/100 ml.
[4] Predicted, mg/100 ml.
[5] Deviation, mg/100 ml.
[6] Diamine antioxidant.
[7] Phenol antioxidant.

Table C–6.—*Inorganic residue correlation*

Sample	Inorganic residue, 16 hr, 200° F	Inorganic residue in 110° F storage											
		8 weeks			8 weeks			16 weeks			32 weeks		
		D[1]	P[2]	Dev[3]	D[1]	P[2]	Dev[3]	D[1]	P[2]	Dev[3]	D[1]	P[2]	Dev[3]
BOG–185 + TEL	10.3	0	0	0	0.2	0	0.2	1.6	15.3	13.7	32.2	36.3	4.1
BOG–186 + TEL	.58	.1	0	.1	0	0	0	5.2	11.0	5.8	24.2	32.5	8.3
BOG–202 + TEL	4.3	0	0	0	3.9	0	3.9	10.8	9.1	1.7	29.0	29.6	.6
BOG–295 + TEL	12.9	0	0	0	0	0	0	13.2	16.6	3.4	21.7	37.2	15.5
BOG–185 + TEL + DA[4]	3.4	0	0	0	.1	0	.1	4.8	7.6	2.8	41.3	19.4	21.9
BOG–186 + TEL + DA[4]	1.4	0	0	0	0	0	0	.3	3.6	3.3	21.0	13.0	8.0
BOG–202 + TEL + DA[4]	4.2	0	0	0	3.2	0	3.2	9.1	8.9	.2	26.7	29.2	2.5
BOG–295 + TEL + DA[4]	.1	0	0	0	0	0	0	0	0	0	0	0	0
BOG–185 + TEL + PA[5]	3.3	0	0	0	0	0	0	14.1	14.1	0	34.1	35.6	1.5
BOG–186 + TEL + PA[5]	3.3	0	0	0	0	0	0	7.1	3.3	1.2	27.5	27.2	.3
BOG–202 + TEL + PA[5]	5.2	0	0	0	3.2	0	3.2	10.1	10.4	.3	35.6	31.7	3.9
BOG–295 + TEL + PA[5]	0	0	0	0	0	0	0	0	0	0	0	0	0

[1] Determined, mg/100 ml.
[2] Predicted, mg/100 ml.
[3] Deviation, mg/100 ml.
[4] Diamine antioxidant.
[5] Phenol antioxidant.

Table C–7.—*Test properties of fuels from 110° F and 200° F stability tests*

Gasoline test properties[1]	Fresh sample	Storage at 110° F: 8 weeks	16 weeks	32 weeks	52 weeks	16-hr oven test, 200° F
Gasoline No. 1:						
Total gum	1.7	2.7	5.7	10.2	19.9	5.7
Precipitate	.0	.5	4.8	10.7	20.3	2.4
Oxygen	21.0					17.6
Gasoline No. 2:						
Total gum	1.1	2.4	5.7	63.6	148	10.1
Precipitate	.0	.4	1.0	9.5	84.4	1.2
Oxygen	21.0					2.7
Gasoline No. 3:						
Total gum	7.7	8.9	8.6	11.3	56.9	10.8
Precipitate	.1	.1	.4	3.0	19.5	1.6
Oxygen	21.0					16.3
Gasoline No. 4:						
Total gum	1.3	2.0	2.6	7.6	97.3	3.5
Precipitate	.0	.1	.2	1.4	9.6	.3
Oxygen	21.0					18.0
Gasoline No. 5:						
Total gum	2.3	3.1	4.9	11.5	10.1	7.4
Precipitate	.0	.0	.4	11.0	32.3	4.9
Oxygen	21.0					17.7
Gasoline No. 6:						
Total gum	1.3	1.7	2.2	4.4	72.5	3.0
Precipitate	.1	.1	.1	.2	17.9	.3
Oxygen	21.0					20.3
Gasoline No. 7:						
Total gum	3.4	5.6	8.1	19.8	63.3	12.5
Precipitate	.1	.3	.7	2.3	23.1	1.6
Oxygen	21.0					15.4
Gasoline No. 8:						
Total gum	3.0	4.4	6.6	11.8	29.2	9.3
Precipitate	.2	.1	.5	1.2	5.3	1.2
Oxygen	21.0					16.7
Gasoline No. 9:						
Total gum	2.9	10.0	11.0	31.3	68.5	11.6
Precipitate	.2	11.6	19.0	29.1	65.1	7.1
Oxygen	21.0					10.4
Gasoline No. 10:						
Total gum	2.3	5.1	7.3	45.1	95.6	7.8
Precipitate	.1	1.5	3.2	13.2	60.4	2.4
Oxygen	21.0					10.8
Gasoline No. 11:						
Total gum	1.3	3.0	4.0	10.2	63.3	6.3
Precipitate	.1	.7	2.0	5.0	28.4	1.9
Oxygen	21.0					15.3
Gasoline No. 12:						
Total gum	2.3	4.3	9.6	102	161	14.4
Precipitate	.0	.2	.9	18.3	67.0	1.0
Oxygen	21.0					1.2
Gasoline No. 13:						
Total gum	1.6	1.7	1.6	2.3	6.4	3.1
Precipitate	.0	.1	.1	.1	3.9	.4
Oxygen	21.0					20.3
Gasoline No. 14:						
Total gum	3.0	3.4	3.7	5.3	8.5	7.5
Precipitate	.1	.1	.1	.4	5.3	.6
Oxygen	21.0					20.3
Gasoline No. 15:						
Total gum	2.4	3.3	5.1	12.3	38.6	4.5
Precipitate	.0	.1	.2	2.2	17.2	.2
Oxygen	21.0					20.1
Gasoline No. 16:						
Total gum	2.5	1.9	2.9	3.4	6.3	2.9
Precipitate	.0	.1	.1	.1	6.4	.2
Oxygen	21.0					21.0
Gasoline No. 17:						
Total gum	0.9	1.9	3.5	8.2	12.3	5.1
Precipitate	.1	.1	.5	3.7	15.6	2.2
Oxygen	21.0					17.7
Gasoline No. 18:						
Total gum	1.9	2.1	3.7	10.3	13.3	7.1
Precipitate	.1	.1	.4	5.5	25.2	4.5
Oxygen	21.0					15.3
Gasoline No. 19:						
Total gum	1.5	2.1	3.9	8.4	12.6	4.6
Precipitate	.0	.2	.4	3.3	15.3	2.0
Oxygen	21.0					16.9
Gasoline No. 20:						
Total gum	1.5	4.0	5.0	10.3	15.0	6.7
Precipitate	.1	.4	1.0	10.3	28.5	6.4
Oxygen	21.0					12.9
Gasoline No. 21:						
Total gum	1.2	1.3	2.9	5.0	10.3	4.0
Precipitate	.1	.0	.1	1.1	8.1	1.3
Oxygen	21.0					13.3
Gasoline No. 22:						
Total gum	3.4	5.1	5.2	10.5	16.0	6.9
Precipitate	.0	.1	.5	5.0	14.9	2.6
Oxygen	21.0					14.9
Gasoline No. 23:						
Total gum	1.0	2.7	2.6	3.7	3.3	2.2
Precipitate	.0	.1	.2	.3	2.6	.3
Oxygen	21.0					20.3
Gasoline No. 24:						
Total gum	1.3	4.7	4.7	6.3	3.4	3.4
Precipitate	.0	.2	.3	.4	.5	.3
Oxygen	21.0					20.1

[1] Gum and precipitate in mg/100 ml of fuel, oxygen in pct. Oxygen not determined for 110° F storage test.

Table C–8.—*Statistical data for analyzing differences between determined and predicted values* [1]

Period of storage	Total gum			Precipitate		
	8 weeks	16 weeks	32 weeks	8 weeks	16 weeks	32 weeks
Σ Differences[2]	18.09	31.59	614.92	14.35	29.42	442.33
Average difference, X_d	−0.343	0.239	−0.096	−0.726	−0.348	0.857
s_d^2	0.6989	1.376	27.942	0.1011	1.211	19.339
s_d	0.836	1.17	5.29	0.318	1.10	4.40
t	2.074	2.074	2.074	2.074	2.074	2.074
u	0.362	0.506	2.29	0.138	0.476	1.90

[1] Supporting data:

$$s_d^2 = \frac{n\Sigma \text{ Diff.}^2 - (\Sigma \text{ Diff.})^2}{n(n-1)}, \text{ where } n = 23.$$

Table C–9.—*Statistical "u" test for differences between determined and predicted values of gum and precipitate*

	X_d	"u"	Conclusion
Gum:			
8 weeks	0.343	0.362	Determined values do not differ from predicted.
16 weeks	.239	.506	Do.
32 weeks	0.96	2.29	Do.
Precipitate:			
8 weeks	.726	.138	Determined values do differ from predicted.
16 weeks	.348	.476	Determined values do not differ from predicted.
32 weeks	.857	1.90	Do.

NOTE.—If the average difference, X_d, is less than "u," conclude that on the average, the determined values do not differ from predicted values. For the "u" test, the algebraic sign of X_d is disregarded.

APPENDIX D.—DATA DERIVED FROM THE STUDY OF FUEL COMPOSITION AND FUEL COMPONENT REACTIVITY AS RELATED TO GUM-FORMING MECHANISMS

The data obtained from a radiotracer study of three-component reaction systems containing a sulfur compound and an olefin in an inert base stock are included in this appendix as support for conclusions discussed in the body of this bulletin. These data are shown in table D–1 through D–3 and include elemental composition of gums formed in these systems.

Table D–4 shows data obtained in a study of molecular weights described by two gum-recovery techniques.

The efforts to develop a gas chromatographic method of analysis for determining existent gum in aged fuels and blends provided information that is discussed in the text of this bulletin and shown in detail in tables D–5 through D–10.

The final phase of these studies included an investigation of TEL reaction mechanisms. Table D–11 shows data obtained from a series of binary reaction systems that were thermally stressed. Table D–12 contains data showing elemental composition of some lead precipitates obtained in the course of these investigations.

Figures D–1 through D–3 show gas chromatograms obtained in the quest for identification of organolead intermediate reaction products in TEL reactions in hydrocarbon systems.

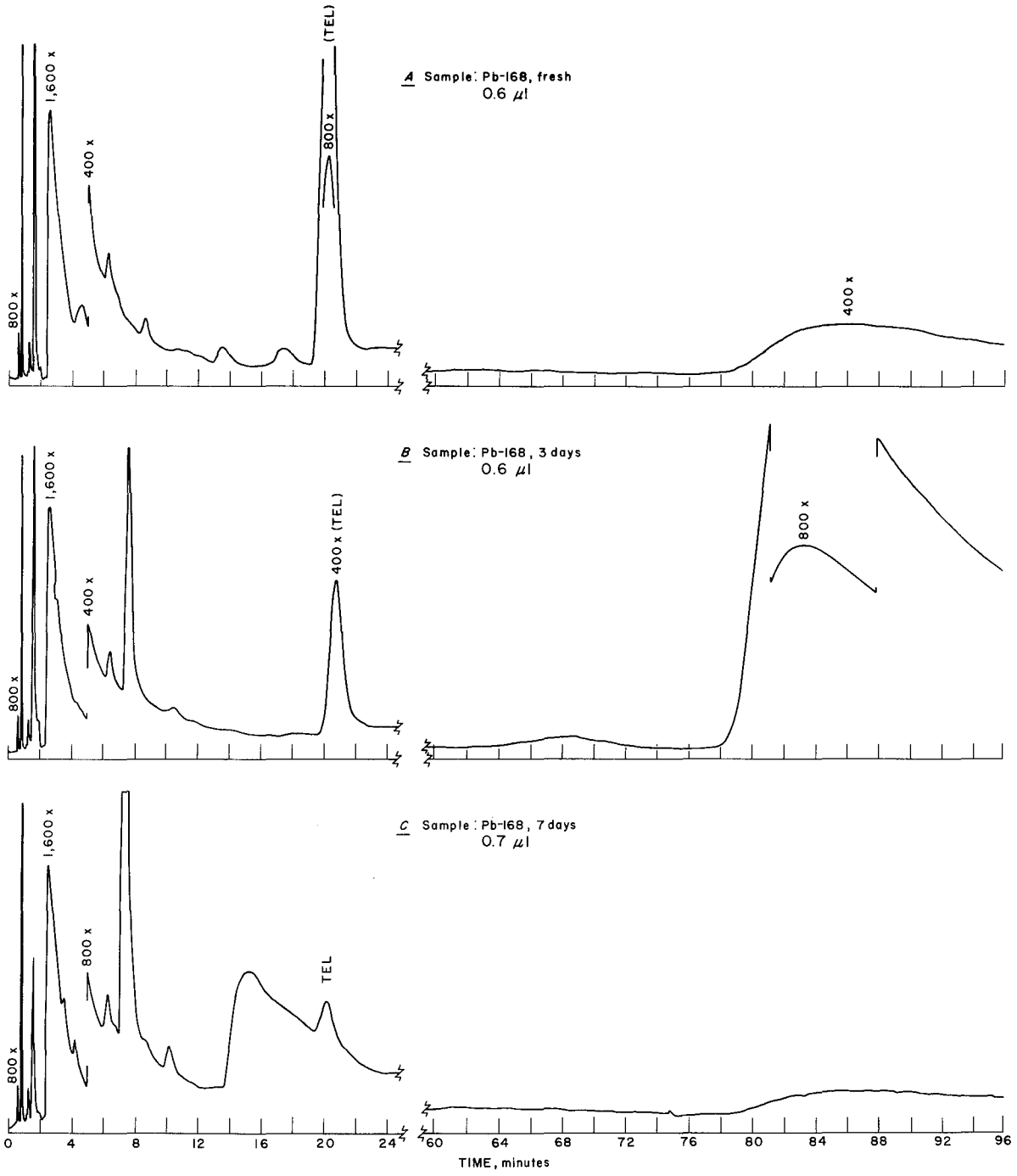


Figure D–1.—Effect of 180° F Storage on a Leaded Binary Hydrocarbon Blend as Defined by Chromatographic Analysis.

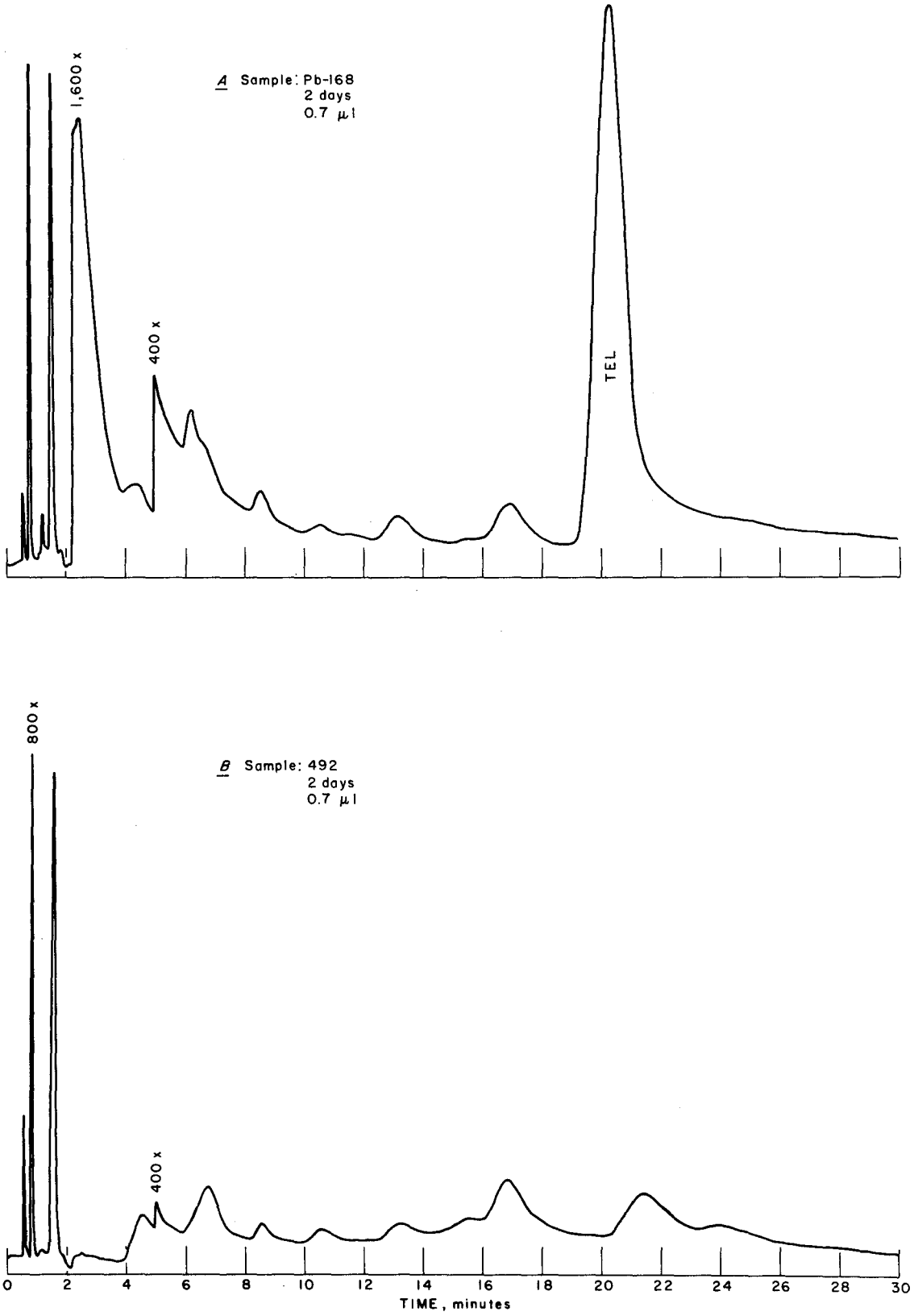


Figure D–2.—The Effect of TEL Upon a Binary Hydrocarbon Reaction Mixture.

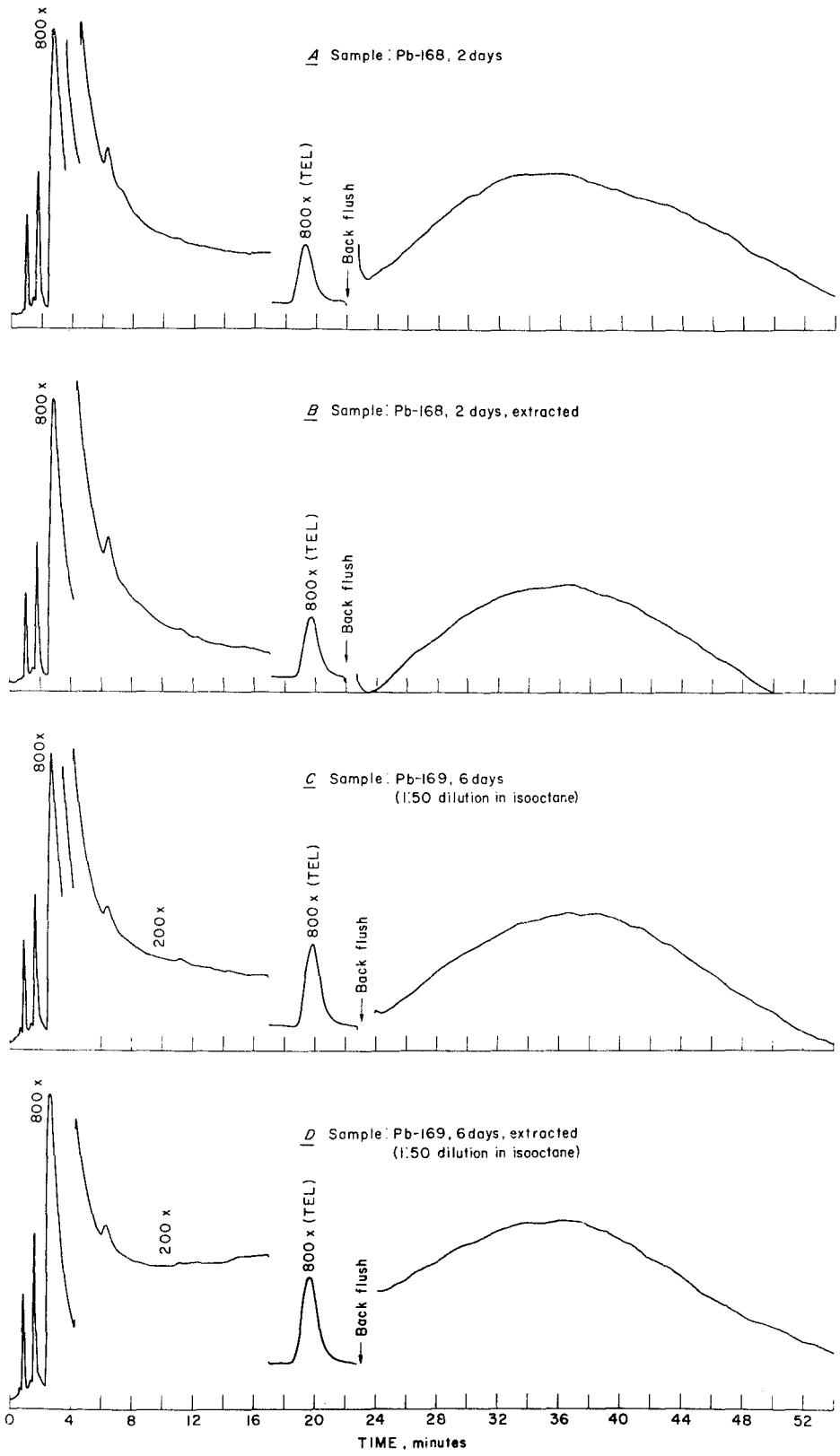


Figure D–3.—Chromatographic Separation of Reaction Mixtures Before and After Extraction of Soluble Alkyllead Salts.

Table D–1.—*GLC separation of reacted ^{35}S-labeled thiophenol in gasoline*

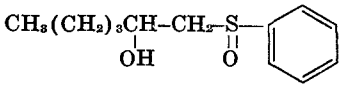
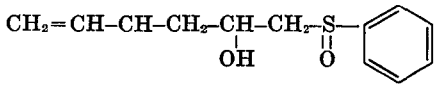
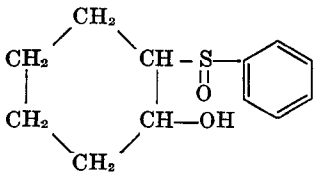
Sample	Days of storage at 110° F	Thiophenol reacted, pct	Air-jet gum, mg/100 ml	
			8 weeks	16 weeks
185[35]	Initial	2.55	5.6	10.5
	1	29.76		
	4	53.75		
186[35]	Initial	3.08	2.0	2.5
	1	49.70		
	5	54.00		
192[35]	Initial	2.26	--	--
	4	3.69		
	7	4.46		
195[35]	Initial	1.77	2.6	11.8
	4	38.10		
	7	39.61		
196[35]	Initial	9.63	0.7	20.1
	4	54.59		
198[35]	Initial	6.34	4.7	7.1
	1	47.92		
	5	46.62		
199[35]	Initial	4.49	1.0	3.9
	2	47.26		
	5	37.12		
204[35]	Initial	5.16	9.8	12.5
	2	60.69		
	5	53.04		

Table D–2.—*Elemental analysis of gums recovered after extended oxidation with air replenishment, pct (32 days at 110° F)*

Composition of 3-component mixture[1]	Carbon	Hydrogen	Sulfur	Oxygen	Total	Mol wt
Thiophenol-hexene-1-*n*-heptane	65.24	7.98	14.48	11.67	99.37	244
Thiophenol-1,5-hexadiene-*n*-heptane	63.26	7.69	13.12	14.16	99.23	252, 267
Thiophenol-1-phenylbutene-2-*n*-heptane	71.19	6.98	6.20	15.25	99.62	314, 300
Thiophenol-cyclohexene-*n*-heptane	65.69	6.34	15.62	12.09	99.74	238
Thiophenol-tetralin-*n*-heptane	73.19	5.87	15.78	4.47	99.31	293
Thiacyclopentane-1-phenylbutene-2-*n*-heptane	75.78	7.98	0.32	16.38	100.46	306

[1] *n*-Heptane, 74.5 vol pct; hydrocarbon, 25.0 vol pct; sulfur compound, 0.5 vol pct.

Table D–3.—*Determined and calculated elemental composition of gums, pct*

Gum source [1]	Carbon	Hydrogen	Oxygen	Sulfur	Mol wt	Postulated structure
GROUP I						
Thiophenol-hexene-1:						
Analysis	65.2	8.0	11.7	14.5	244	
Calculated	63.7	8.0	14.1	14.2	226	
Thiophenol-1,5-hexadiene:						
Analysis	63.3	7.7	14.2	13.1	259	
Calculated	64.3	7.1	14.3	14.3	224	
Thiophenol-cyclohexene:						
Analysis	65.7	6.3	12.1	15.6	238	
Calculated	64.3	7.1	14.3	14.3	224	
GROUP II						
Thiophenol-1-phenylbutene-2:						
Analysis	71.2	7.0	15.3	6.2	307	$C_{18}H_{21}S_{0.75}O_3$
Calculated	74.6	4.6	14.9	5.8	309	
Thiacyclopentane-1-phenylbutene-2:						
Analysis	75.8	8.0	16.4	.3	306	$C_{18}H_{21}S_{0.3}O_3$
Calculated	78.6	4.6	16.4	.3	295	
Thiophenol-tetralin:						
Analysis	73.2	5.9	4.5	15.8	293	$C_{18}H_{18}S_{1.5}O_{0.75}$
Calculated	72.7	6.7	4.5	15.7	286	

[1] Mixture composition:
n-Heptane, 74.5 vol pct; hydrocarbon, 25.0 vol pct; sulfur compound, 0.5 vol pct.

Table D–4.—*Distribution of selected hydrocarbons in vapor transfer products* [1] *and in air-jet evaporation*

Sample [2]	Evaporation method	Mol wt	Pct in distillate	Pct in residue
2-Nonadecene	Vapor transfer	266	7.5	92.5
Dodecyl toluene	Do.	261	22.1	77.9
Octadecene	Do.	252	11.6	88.4
Dodecyl benzene	Do.	246	13.5	86.5
Hexadecane	Do.	226	18.8	81.2
Four-component mixture:				
Octadecene	Do.	242	19	81
Hexadecane	Do.	226	35	65
Tetradecane	Do.	198	86	14
Dodecene	Do.	168	100	0
C_{16} hexadecane	Air jet	226	100	0
C_{19} nonadecene	Do.	266	99	1
C_{22} docosane	Do.	310	68	32
C_{24} tetracosane	Do.	339	61	39
C_{28} octacosane	Do.	395	16	84

[1] "Standard" transfer finished at 95 μ mercury (Hg) pressure.
[2] 0.20 gram of compound in 200 ml of *n*-heptane.

Table D–5.—*GLC backflush peaks in gasoline stocks (C_{19} or higher)*

Sample	Air-jet gum		GLC peak area, ppm		
	Mg/100 ml	Ppm	72-min forward flow, no backflush	16-min forward flow, backflush	72-min forward flow, backflush
RMF–204, fresh	7.7	99	Trace	29	Trace
RMF–204, aged	42.7	547	None	238	18
RMF–205, fresh	1.9	24	Trace	5	None
RMF–205, aged	33.6	432	None	151	40
Garage Gasoline			None	121	9
BOG–185–0	1.5	20	None	23	16
BOG–186–0	1.1	16	None	20	None
BOG–187–0	2.6	36	17	41	24
BOG–187–8	2.3	32	--	[1] 120	--
BOG–190–0	.6	8	7	[1] 185	15
BOG–191–0	.2	3	Trace	[1] 68	140
BOG–193–0	1.0	13	Trace	[1] 113	132
BOG–194–0	0	0	None	[1] 848	68
BOG–195–0	1.0	12	6	[1] 404	105
BOG–196–0	1.7	23	None	[1] 108	82
BOG–198–0	1.6	21	None	19	5
BOG–199–0	.6	9	None	27	4
BOG–202–0	1.8	27	8	[1] 107	18
BOG–202–8	3.6	47	--	[1] 116	--
BOG–202–24 at 250° F [2]	30.6	404	None	[1] 533	158
BOG–202–24 at 250° F [3]	25.6	338	--	[1] 878	--
BOG–185–16	10.5	141	Trace	48	None

[1] GLC ppm much higher than air-jet gum in ppm.
[2] No liner.
[3] Liner.

Table D–6.—*Retention times of pure compounds*

Compound	Mol wt	Retention time, min
Dodecene (C_{12})	168	1
Tetradecane (C_{14})	198	2
Hexadecane (C_{16})	226	4
Octadecane (C_{18})	254	8
Nonadecene (C_{19})	266	15
Docosane (C_{22})	310	32.5
Tetracosane (C_{24})	339	68
Octacosane (C_{28})	395	72+

Table D–7.—*16-minute backflush peak areas, ppm; duplicates on same internal standard mix*

< 100 ppm			100–200 ppm			200–300 ppm			300–400 ppm			> 400 ppm		
1st run	2d run	d [1]	1st run	2d run	d [1]	1st run	2d run	d [1]	1st run	2d run	d [1]	1st run	2d run	d [1]
20	27	7	190	180	10	270	288	18	315	381	66	401	407	6
40	42	2	101	125	24	284	300	16	379	374	5	466	441	25
79	66	13	98	118	20	205	214	9	304	308	4	456	467	11
18	20	2	93	112	19	217	219	2	366	338	28	409	440	31
63	78	15	100	120	20	273	293	20	343	356	13	488	500	12
84	57	27	125	127	2	287	280	7				556	590	34
96	78	18	175	171	4	224	241	17						
18	16	2	182	192	10	231	298	67						
56	54	2	166	181	15	233	249	16						
30	33	3	96	117	21									
66	58	8	148	188	40									
15	26	11	175	149	26									
7	12	5	101	115	14									
45	42	3	139	152	13									
95	95	0	178	191	13									
86	74	12	149	170	21									
14	16	2	131	145	14									
8	7	1	121	150	29									
10	24	14	162	179	17									
25	33	8	134	186	2									
$n = 20$			$n = 20$			$n = 9$			$n = 5$			$n = 6$		
$\Sigma d^2 = 2{,}149$			$\Sigma d^2 = 7{,}204$			$\Sigma d^2 = 6{,}148$			$\Sigma d^2 = 5{,}350$			$\Sigma d^2 = 3{,}043$		
$^2s = \sqrt{\frac{2{,}149}{40}}$			$^2s = \sqrt{\frac{7{,}204}{40}}$			$^2s = \sqrt{\frac{6\,148}{18}}$			$^2s = \sqrt{\frac{5{,}350}{10}}$			$^2s = \sqrt{\frac{3{,}043}{12}}$		
$s = \sqrt{53.725}$			$s = \sqrt{180.10}$			$s = \sqrt{341.55}$			$s = \sqrt{535}$			$s = \sqrt{253.58}$		
$s = 7.33$			$s = 13.42$			$s = 18.49$			$s = 23.15$			$s = 15.92$		

[1] Difference.
[2] Standard deviation.

Table D–8.—*16-minute backflush peak areas, ppm; repeated runs on same fuel, different internal standard mix and sample*

BOG–185		BOG–190		BOG–193		BOG–194		BOG–195		BOG–196		BOG–202	
Peak	x [1]	Peak	x [1]	Peak	x [1]	Peak	x [1]	Peak	x [1]	Peak	x [1]	Peak	x [1]
18	6	288	60	14	1			45	4	59	4	96	13
27	3	190	38	20	5			49	0	84	29	93	10
18	6	256	28	14	1	183	10	37	12	57	2	87	4
17	7			14	1	192	1	40	9	57	2	62	21
21	3	202	26	7	8	173	20	53	4	26	29	86	3
21	3	201	27	28	13	198	5	72	23	71	16	100	17
39	15	195	33	11	4	169	24	71	22	48	7	45	38
21	3	242	14	10	5	230	37	55	6	25	30	100	17
46	22	209	19	13	2	203	6	45	4	70	15	76	7
21	3	270	42	19	4	181	12	49	0	32	23		
19	5	227	1	22	7	209	16	37	12	59	4		
				8	7			40	9	57	2		
				19	4			53	4	57	2		
				10	5			57	8	26	29		
				14	1			37	12	71	16		
				11	4			45	4	48	7		
				10	5					99	44		
				13	2					35	20		
				19	4					93	38		
				22	7					26	29		
$n = 11$		$n = 10$		$n = 20$		$n = 9$		$n = 16$		$n = 20$		$n = 9$	
Avg = 24		Avg = 228		Avg = 15		Avg = 193		Avg = 49		Avg = 55		Avg = 83	
$\Sigma x^2 = 900$		$\Sigma x^2 = 10{,}644$		$\Sigma x^2 = 572$		$\Sigma x^2 = 2{,}907$		$\Sigma x^2 = 1{,}787$		$\Sigma x^2 = 9{,}456$		$\Sigma x^2 = 2{,}806$	
$^2s = \sqrt{\frac{900}{10}}$		$^2s = \sqrt{\frac{10{,}644}{9}}$		$^2s = \sqrt{\frac{572}{19}}$		$^2s = \sqrt{\frac{2{,}907}{8}}$		$^2s = \sqrt{\frac{1{,}787}{15}}$		$^2s = \sqrt{\frac{9{,}456}{19}}$		$^2s = \sqrt{\frac{2{,}806}{8}}$	
$s = \sqrt{90}$		$s = \sqrt{1{,}182.67}$		$s = \sqrt{30.10}$		$s = \sqrt{363.38}$		$s = \sqrt{119.13}$		$s = \sqrt{497.68}$		$s = \sqrt{350.75}$	
$s = 9.5$		$s = 34.39$		$s = 5.49$		$s = 19.06$		$s = 10.91$		$s = 22.31$		$s = 18.73$	

[1] Deviation from average.
[2] Standard deviation.

Table D–9.—*16-minute backflush peak areas, ppm, and gum level of fuels aged in bomb*

Sample	Bomb temp, ° F	16-minute backflush, ppm			Total gum, mg/100 ml
		Fresh	Aged	Difference	
		16-HR TESTS			
BOG–185	300	19	334	315	48
BOG–185	250	19	179	160	43
BOG–185	200	19	91	72	13
BOG–185	150	19	23	4	3
BOG–193	300	15	306	291	35
BOG–193	250	15	192	177	23
BOG–193	200	15	128	113	14
BOG–193	150	15	18	3	6
BOG–195	300	45	349	304	40
BOG–195	250	45	169	124	22
BOG–195	200	45	112	67	10
BOG–195	150	45	65	20	5
BOG–196	300	53	412	359	34
BOG–196	250	53	311	258	22
BOG–196	200	53	171	118	21
BOG–196	150	53	48	0	7
BOG–202	300	76	470	394	59
BOG–202	250	76	434	358	37
BOG–202	200	76	181	105	10
BOG–202	150	76	89	13	6
		8-HR TESTS			
BOG–185	300	19	218	199	17.3
BOG–185	250	19	146	127	19.5
BOG–185	200	19	60	41	4.2
BOG–185	150	19	---	---	--
BOG–193	300	15	350	335	20.3
BOG–193	250	15	185	170	23.7
BOG–193	200	15	66	51	3.6
BOG–193	150	15	---	---	--
BOG–195	300	45	276	231	27.4
BOG–195	250	45	160	110	10.0
BOG–195	200	45	136	91	2.5
BOG–195	150	45	---	---	--
BOG–196	300	53	425	372	24.9
BOG–196	250	53	283	230	26.6
BOG–196	200	53	284	231	16.2
BOG–196	150	53	---	---	--
BOG–202	300	76	494	418	36.4
BOG–202	250	76	433	357	11.7
BOG–202	200	76	264	188	1.4
BOG–202	150	76	---	---	--

Table D–10.—*16-minute backflush peak areas, ppm, and gum level of fuels aged at 110° F*

Sample	Weeks at 110° F	16-minute backflush, ppm			Total gum, mg/100 ml
		Fresh	Aged	Difference	
BOG–185	0	19	---	---	1.9
BOG–185	3	19	20	1	3.2
BOG–185	8	19	59	40	5.4
BOG–185	16	19	107	88	11.1
BOG–185	32	19	184	165	15.9
BOG–193	0	15	---	---	1.8
BOG–193	3	15	12	0	2.0
BOG–193	8	15	62	47	4.4
BOG–193	16	15	152	137	6.5
BOG–193	32	15	180	165	9.2
BOG–195	0	45	---	---	1.6
BOG–195	3	45	63	18	3.2
BOG–195	8	45	230	185	3.9
BOG–195	16	45	305	260	3.9
BOG–195	32	45	373	328	5.0
BOG–196	0	53	---	---	3.5
BOG–196	3	53	57	4	9.1
BOG–196	8	53	303	250	13.6
BOG–196	16	53	[1] 468	415	13.9
BOG–196	32	53	389	336	13.1
BOG–202	0	76	---	---	1.4
BOG–202	3	76	124	48	2.5
BOG–202	8	76	548	472	4.0
BOG–202	16	76	1485	1409	7.4
BOG–202	32	76	618	542	9.3

[1] Erratic baseline, poorly defined peak.

Table D–11.—*Data from oven tests of leaded binary hydrocarbon blends*

Hydrocarbon [1]	40-hr test at 180° F						
	Sample No. of blend	Precipitate, mg/100 ml	Soluble gum, mg/100 ml	Insoluble gum, mg/100 ml	Total gum, mg/100 ml	Oxygen remaining, pct	Approximate purity, pct [1]
Isooctane (base)	Pb– 74	1.4	0.9	1.7	2.6	----	99.9
	Pb– 78	.8	1.0	1.5	2.5	----	99.9
	Pb– 80	2.0	.8	1.8	2.1	----	99.9
	Pb– 96	3.2	.9	1.9	2.8	20.0	99.9
	Pb–141	.8	.2	1.0	1.2	----	99.9
	Pb–148	1.2	.5	1.5	2.0	20.7	99.9
n-Hexane	Pb– 88	2.3	.9	1.3	2.2	20.1	----
Cyclohexone	Pb–135	.7	.4	1.8	2.2	20.8	99+
Methylcyclohexane	Pb–109	2.0	1.1	1.6	2.7	20.3	----
Ethylcyclopentane	Pb–107	3.5	.6	1.0	1.6	20.0	99+
n-Decane	Pb–140	1.0	.5	1.9	2.4	----	99.9
1-Hexene	Pb–159	1.4	.9	1.7	2.6	20.5	98.8
1-Heptene	Pb–112	2.8	1.0	1.7	2.7	20.1	----
1-Octene	Pb–153	1.2	1.5	1.1	2.6	20.6	99.9
1-Nonene	Pb–113	2.0	.1	1.5	1.6	20.3	----
4-Methylpentene-1	Pb–147	2.2	.5	2.3	2.8	20.4	99.9
2-Methylhexene-2	Pb–154	2.2	1.1	2.2	3.3	20.1	99.9
Cyclohexene	Pb–114	8.9	2.2	2.8	5.0	16.3	99.8
	Pb–157	6.0	1.0	3.7	4.7	17.6	99.9
1-Ethylcyclopentene	Pb–134	22.0	2.5	2.3	4.8	8.5	99.9+
1,2-Dimethylcyclopentene	Pb–160	20.3	4.8	2.2	7.0	6.0	99.14
1,2-Dimethylcyclohexene	Pb–150	15.8	5.8	.9	6.7	8.5	----
	Pb–151	17.5	6.5	1.5	8.0	7.9	99.91
1,2,3-Trimethylcyclopentene	Pb–167	16.8	4.7	1.3	6.0	5.5	99.87
3,3,5-Trimethylcyclohexene	Pb–163	1.0	1.3	2.2	3.5	20.7	99.26
4,4-Dimethylcyclohexene	Pb–164	.84	1.1	2.6	3.7	20.7	99.78
2,5-Dimethylhexadiene-1,5	Pb–161	3.6	1.9	2.7	4.6	18.2	95–99.7
Indene	Pb–129	2.9	8.2	1.7	9.9	18.6	99.9+
Indan	Pb–128	2.1	1.6	2.5	4.1	19.8	99.6
Toluene	Pb–101	3.1	.7	1.5	2.2	20.1	----
n-Propylbenzene	Pb–119	1.9	1.9	3.1	5.0	20.6	----
1,2,4-Trimethylbenzene	Pb–115	.8	1.5	1.2	2.7	20.8	99.5
Naphthalene	Pb–145	.8	.8	1.7	2.5	20.5	----
Tetralin	Pb–149	1.5	.9	1.5	2.4	20.1	99.9+
	Pb–152	1.8	.9	1.8	2.7	20.0	99.9+

[1] Purity check by FID gas chromatography.

Table D–12.—*Analyses of lead precipitates from stored fuels and blends*

Sample	Storage history		Elemental analysis, wt pct					
	Time, wk	Temp, °F	Lead	Oxygen	Carbon	Hydrogen	Sulfur	Nitrogen
AMC gasoline:								
1	62	110	59.41	19.75	15.32	1.47	3.48	0.15
2	52	110	55.69	20.36	20.67	2.04	1.76	.11
3	52	110	57.42	19.98	20.26	1.89	1.13	.12
4	52	110	54.12	22.16	20.78	1.95	.97	.15
5	52	110	62.48	18.25	16.78	1.47	.20	.05
6	52	110	51.57	20.23	23.97	2.22	1.04	.17
7	52	110	54.46	21.30	21.06	2.05	1.36	.16
8	52	110	53.76	20.51	22.37	2.12	1.60	.34
9	52	110	54.41	22.02	20.97	1.95	.91	.07
10	52	110	52.49	22.14	22.15	1.96	.66	.12
11	52	110	55.61	20.65	20.40	1.90	.87	.20
12	52	110	56.47	21.54	19.20	1.69	.98	.07
13	52	110	52.42	----	13.63	1.46	---	---
Blend 116 (hexene-1)	0.24 (40 hr)	180	72.6	21.1	6.0	.96	---	---
Blend 132 (1-ethylcyclopentene)	0.24 (40 hr)	180	70.1	19.6	8.9	1.05	---	---
Blend 132 (1-ethylcyclopentene)	0.24 (40 hr)	180	71.5	15.4	7.7	.75	---	---
Blend 132 (1-ethylcyclopentene)	22 (5 mo)	110	59.3	19.2	14.6	1.58	---	---
AMC gasoline 9	.68 (4¾ days)	180	76.8	14.6	6.8	1.94	---	---
Lead precipitates:								
$(C_2H_5)_2PbCO_3$	--	---	63.7	14.8	18.5	3.1	---	---
$(C_2H_5)_2Pb(OH)_2$	--	---	69.0	11.0	16.0	4.0	---	---
$2\,PbCO_3 \cdot Pb(OH)_2$	--	---	80.0	16.5	3.0	.3	---	---
$PbCO_3$	--	---	92.8	7.2	0	0	---	---

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