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Oven Test for Prediction of Gasoline Storage Stability

UNITED STATES DEPARTMENT OF THE INTERIOR

BUREAU OF MINES

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Oven Test for Prediction of Gasoline Storage Stability

By Frank G. Schwartz, Charles S. Allbright, and Cecil C. Ward

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UNITED STATES DEPARTMENT OF THE INTERIOR
Stewart L. Udall, Secretary

BUREAU OF MINES
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STORAGE STABILITY OF GASOLINE

Oven Test for Prediction of Gasoline Storage Stability

by

Frank C. Schwartz,[1] Charles S. Allbright,[2] and Cecil C. Ward[3]

ABSTRACT

The Bureau of Mines developed a rapid test method for predicting the stability of motor gasoline during long-term storage. The amounts of gum and inorganic residue formed in 13 gasolines during a 16-hour oven test at 200° F were compared with the amounts formed in the same gasolines stored at 110° F, and analyzed following 8-, 16-, 32-, 44-, and 52-week storage periods. Satisfactory methods were developed for predicting gum and inorganic residue formation during fuel storage periods as long as 32 weeks at 110° F, the approximate equivalent of 5.7 years at 80° F. The only data required to apply the methods are the amount of gum and inorganic residue formed, and the amount of oxygen that reacted, during a 16-hour oven test. A direct relationship existed between inorganic residue formed during the oven test and during 110° F storage. Statistical treatment of the data showed predicted values were as reliable as determined values.

By use of a modified Arrhenius equation, the 110° F storage time can be extrapolated to equivalent time at any temperature below 110° F. ~~Thus~~ by combining the stability prediction method with the mathematical extrapolation, the storage performance of motor gasoline for extended periods can be estimated at any temperature up to 110° F.

INTRODUCTION

Modern refining methods and the use of antioxidants provide motor gasolines that resist deterioration during several months of storage, but most gasolines will deteriorate if subjected to longer storage periods (4-5, 7).[4] Thus, gasoline deterioration is not a major problem for the refiner in providing gasoline for the motoring public, because stocks are usually consumed

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[4] Underlined numbers in parentheses refer to items in the list of references preceding the appendixes.

within a few weeks after they are manufactured; however, gasoline deterioration is a problem for the armed services, because they must store gasolines throughout the world, that may be in storage for 3 to 5 years and that must be suitable for use when needed. Standard methods (2-3) are available for measuring the existent gum in the gasoline as received and the resistance of the gasoline to oxidation, but there has been no reliable rapid test procedure for predicting the extent of fuel deterioration during storage. Therefore, the Army Materiel Command, Department of the Army, is sponsoring a research program at the Bartlesville Petroleum Research Center of the Bureau of Mines to study the fundamental causes of fuel instability and to provide information that might be used to develop a reliable stability prediction method. The data discussed in this report are a part of that research program.

Some gasolines oxidize during prolonged storage, forming precipitates as well as gasoline-soluble products that cause discoloration of the gasolines. The gasoline-soluble oxidation products may appear as a hard or sticky residue after fuel evaporation. This residue, called soluble gum, may deposit in the induction systems of an engine with deleterious effects. Some of the precipitate may be entrained during use, causing physical plugging of filters, valves, and orifices. The portion of the precipitate that is soluble in a mixture of equal parts of benzene, methanol, and acetone (but not gasoline) is called insoluble gum, and the remaining precipitate is referred to as inorganic residue.

The storage stability of each gasoline used in this investigation was initially determined by storing 12 samples of each gasoline in closed glass bottles in a test room maintained at 110° F; at selected intervals, the aged gasolines were analyzed for gum and precipitate formation. The 110° F temperature increases the rate of gum formation in the fuels several times beyond the rate obtained at ambient temperature storage. Calculations using a modified version of the Arrhenius equation (8) indicate that 1 week of 110° F storage is equivalent to about 9.2 weeks storage at 80° F. Storage at 110° F, while reliable, is time consuming and sometimes requires as long as 8 months for complete stability evaluation.

In the present study, an accelerated stability test for gasolines has been devised in which aging of the fuel for 16 hours at 200° F in a laboratory oven has enabled prediction of gum and precipitate formation in motor gasolines stored at 110° F for any period up to 32 weeks.

EXPERIMENTAL PROCEDURE AND RESULTS

Procedure

The data reported here were obtained on a group of samples of 13 motor gasolines, including commercial and military gasolines. These samples were subjected to 110° F storage tests and to 200° F oven tests to obtain data used to develop correlations between the two test procedures.

The 110° F storage tests (see appendix A) were made in amber glass bottles, each with a capacity of 1,200 ml, in which a 350-ml sample was stored.

Deterioration of each gasoline was measured after 8, 16, 32, 44, and 52 weeks of storage. At 4-week intervals the samples were cooled and aerated to replenish oxygen.

The oven tests (see appendix B) were made for 16 hours at 200° F with 130 ml of gasoline in 16-ounce pressure-type bottles. The bottles were encased in cylindrical safety shields (fig. 1) for protection of personnel in case of breakage. 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 2.

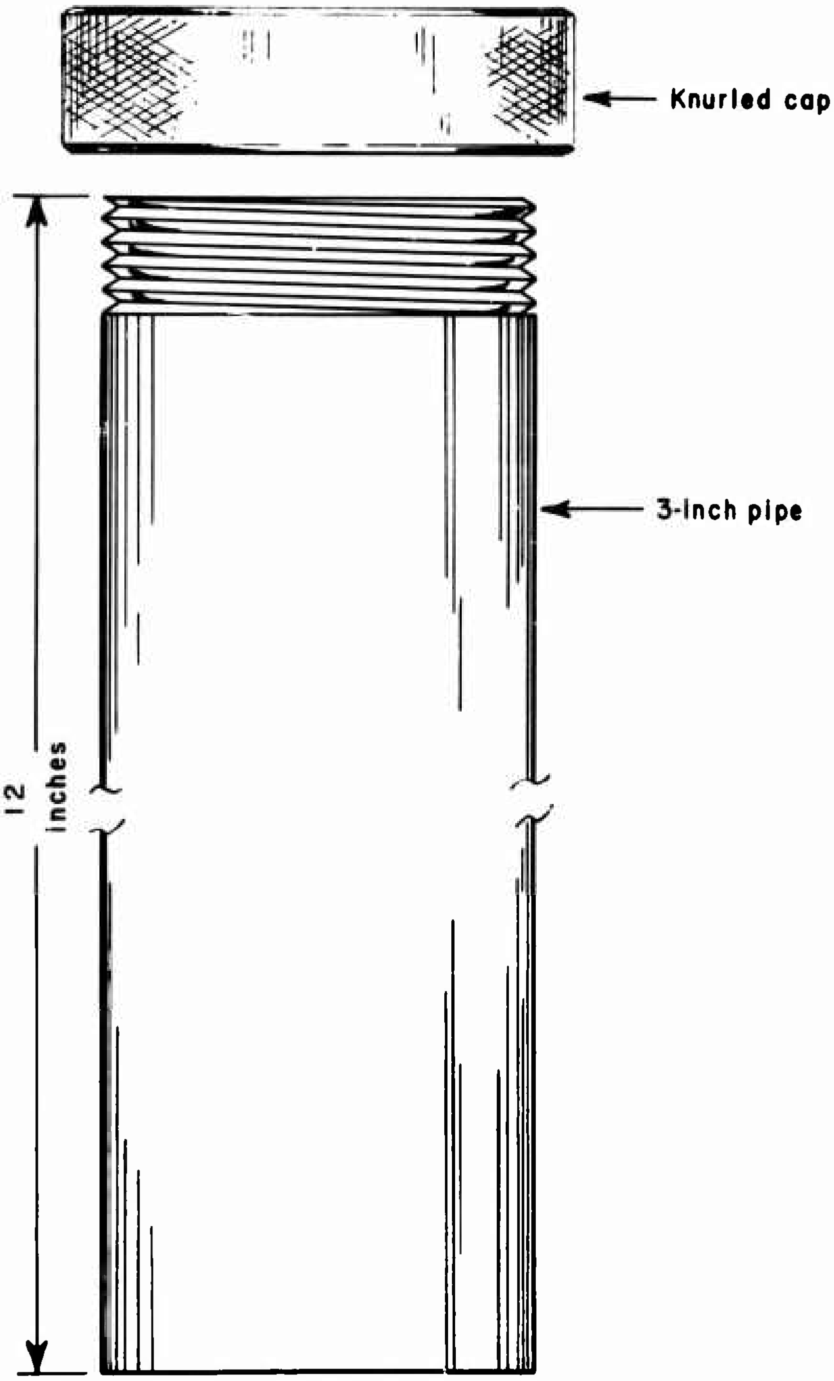

FIGURE 1. - Metal Safety Shield for Beverage Bottle Oven Test.

Fuel deterioration in both storage and oven tests was measured by determination of inorganic residue, insoluble gum, and soluble gum, all in mg/100 ml; 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, soluble (air-jet) gum was determined on the filtrate by ASTM Method (2, pp. 166-172). Insoluble gum was removed from the inorganic residue by washing the filter with a solvent consisting of equal parts of benzene, methanol, and acetone.

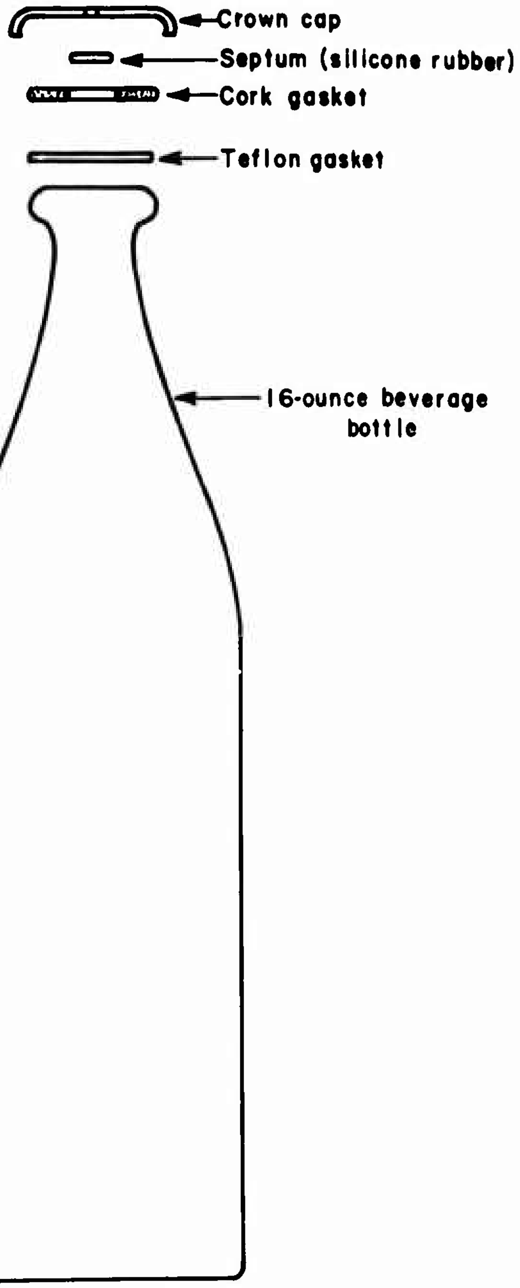

FIGURE 2. - Beverage Bottle and Cap.

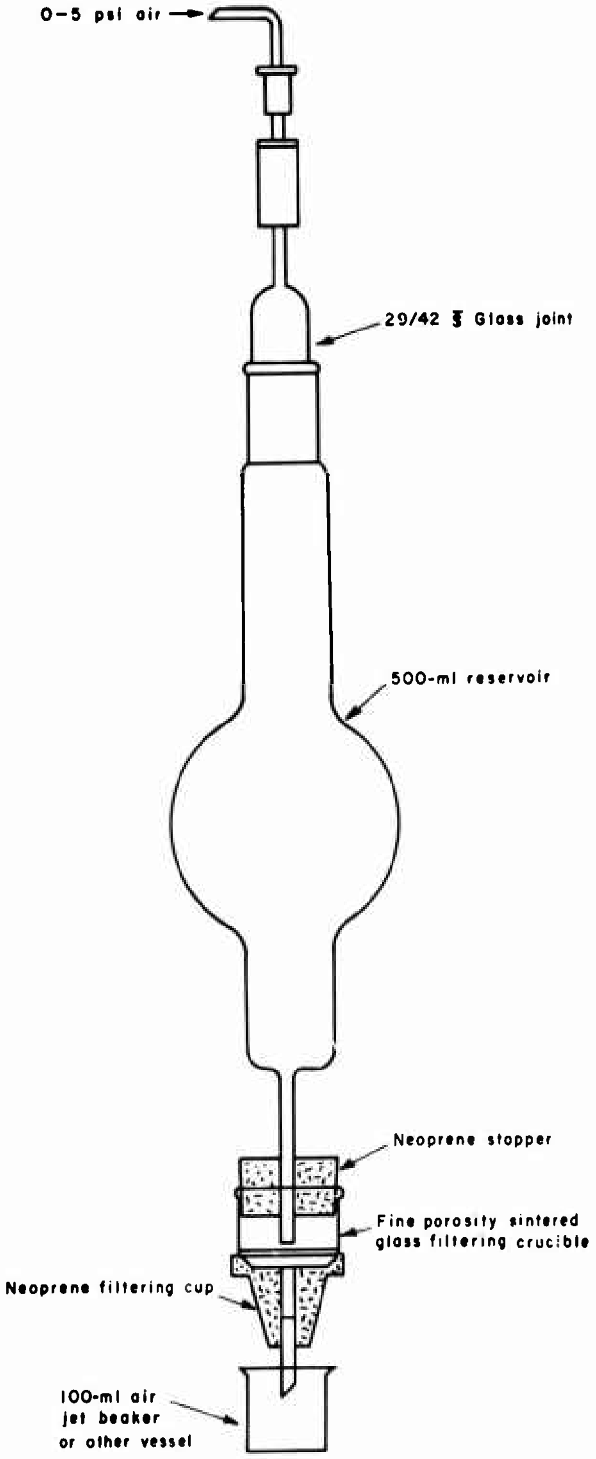

FIGURE 3. - Filtering Assembly.

The solvent was evaporated 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 3.

The outage of the bottle used in the oven test procedure was sampled (see appendix C) through the septum by using a chromatographic microliter hypodermic syringe; a sample was withdrawn and charged to a gas chromatograph. 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.

The initial properties of unaged samples of the 13 gasolines, as well as all information available as to type of gasoline and lead content, are given in table 1.

TABLE 1. - Initial tests on gasolines

Gasoline	1	2	3	4	5	6	7	8	9	10	11	12	13
Supplier	Commercial	Commercial	Military	Commercial	Military	Commercial	Military	Military	Military	Military	Military	Commercial	Military
Type fuel	-	-	MIL-G-3056B	-	-	-	Combat type.	Combat type.	Combat type.	Combat type.	Combat type.	-	MIL-G-3056B
Fill date	-	-	-	-	-	-	Feb. 1965	May 1965	Feb. 1966	Nov. 1966	Feb. 1967	-	-
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	52.3
Distillation, ° F:[1]													
Initial boiling point	93	88	98	98	100	82	100	112	102	98	102	84	96
10 pct recovered	119	128	140	121	148	114	146	146	142	144	144	122	148
50 pct recovered	203	240	224	179	218	224	214	212	216	220	222	206	234
90 pct recovered	338	372	328	319	302	356	352	348	314	328	332	326	324
End point	423	480	404	414	362	402	406	402	378	402	410	390	406
Sulfur....wt pct	0.06	0.021	0.017	0.031	0.020	0.012	0.041	0.039	0.016	0.019	0.019	0.027	0.006
Composition, pct:[2]													
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	59.0
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	0.0
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	41.0
Induction period min[3]	1,440	483	720 (1964)	679	-	754	-	-	-	-	-	332	>5,040
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	1.54

[1] ASTM D86.

[2] ASTM D1319.

[3] ASTM D525.

Twelve bottles of each gasoline were stored at 110° F. Two bottles of each were removed for analysis after periods of 8, 16, 32, 44, and 52 weeks to obtain basic information as to the storage performance of the gasolines. The average results of these storage tests are listed in table 2.

TABLE 2. - 110° F storage data, mg/100 ml[1]

Gasoline	Inorganic residue	Insoluble gum	Soluble gum	Total gum	Inorganic residue	Insoluble gum	Soluble gum	Total gum
	Initial tests				8 weeks' test			
1	0.0	0.4	1.3	1.7	0.5	0.5	2.2	2.7
2	.0	.2	.9	1.1	.4	.5	1.9	2.4
3	.1	.2	7.5	7.7	.1	.4	8.5	8.9
4	.0	.2	1.1	1.3	.1	.4	1.6	2.0
5	.0	.3	2.0	2.3	.0	.3	2.8	3.1
6	.1	.2	1.1	1.3	.1	.2	1.5	1.7
7	.1	.1	3.3	3.4	.3	.3	5.3	5.6
8	.2	.2	2.8	3.0	.1	.3	4.1	4.4
9	.2	.2	2.7	2.9	11.6	1.7	8.3	10.0
10	.1	.3	2.0	2.3	1.5	.7	4.4	5.1
11	.1	.2	1.6	1.8	.7	.6	2.4	3.0
12	.0	.2	2.1	2.3	.2	.6	4.2	4.8
13	.0	.4	1.2	1.6	.1	.2	1.5	1.7
	16 weeks' test				32 weeks' test			
1	4.8	1.0	4.7	5.7	10.7	2.1	8.0	10.1
2	1.0	.7	5.0	5.7	9.5	6.6	57.0	63.6
3	.4	.7	7.9	8.6	3.0	1.2	10.1	11.3
4	.2	.5	2.1	2.6	1.4	1.2	6.4	7.6
5	.4	.4	4.5	4.9	11.0	1.7	9.8	11.5
6	.1	.4	1.8	2.2	.2	.6	3.8	4.4
7	.7	.6	7.5	8.1	2.3	1.8	18.0	19.8
8	.5	.4	6.2	6.6	1.2	1.5	10.3	11.8
9	19.0	2.8	8.2	11.0	29.1	3.3	28.5	31.8
10	3.2	1.1	6.2	7.3	13.2	3.2	41.9	45.1
11	2.0	.7	3.3	4.0	5.0	2.9	7.3	10.2
12	.9	1.5	8.1	9.6	18.8	8.6	93.2	101.8
13	.1	.2	1.4	1.6	.1	.4	1.9	2.3
	44 weeks' test				52 weeks' test			
1	-	-	-	-	20.3	3.0	16.9	19.9
2	[2]11.0	[2]8.1	[2]102.2	[2]110.3	34.4	8.6	139.4	148.0
3	7.5	2.0	31.5	33.5	19.5	4.4	52.5	56.9
4	3.4	7.1	70.0	77.1	9.6	5.8	92.0	97.8
5	27.5	2.9	8.9	11.8	32.3	2.7	7.4	10.1
6	11.2	2.5	50.3	52.8	17.9	1.7	70.8	72.5
7	7.3	2.8	37.0	39.8	23.1	4.8	58.5	63.3
8	2.6	1.3	18.9	20.2	5.3	2.3	26.9	29.2
9	47.0	3.1	55.8	58.9	65.1	3.4	65.1	68.5
10	39.9	4.7	90.4	95.1	60.4	3.9	91.7	95.6
11	13.2	1.4	26.9	28.3	28.4	4.6	58.7	63.3
12	[3]48.5	[3]7.0	[3]95.0	[3]102.0	67.0	8.9	151.7	160.6
13	2.5	.8	2.3	3.1	3.9	1.2	5.2	6.4

[1] Average of duplicate bottle storage.

[2] 42-week storage of gasoline 2.

[3] One bottle only.

Oven tests were made with two different types of 16-ounce beverage bottles, which yielded results that correlated quite well with 110° F storage data. Average results for each oven test are given in table 3. The oven tests were made in duplicate on two different days for each fuel.

TABLE 3. - Oven tests, 16 hours at 200° F in bottles, mg/100 ml

Gasoline	Initial tests				16 hours						
	Inorganic residue	Insoluble gum	Soluble gum	Total gum	Inorganic residue	Insoluble gum	Soluble gum	Total gum	O_2 in air in outage, pct	MF_{16}	O_2 reacted, pct
SET 1											
1	0.0	0.4	1.3	1.7	2.0	1.2	3.8	5.0	17.3	0.58	17.6
2	.0	.2	.9	1.1	1.0	1.3	6.5	7.8	4.0	5.43	81.0
3	.1	.2	7.5	7.7	1.6	1.0	9.3	10.3	17.3	.46	17.6
4	.0	.2	1.1	1.3	.3	.8	2.5	3.3	17.8	.30	15.2
5	.0	.3	2.0	2.3	6.0	.9	5.2	6.1	17.1	.71	18.6
6	.1	.2	1.1	1.3	.1	1.2	2.1	3.3	20.3	.07	3.3
7	.1	.1	3.3	3.4	1.5	1.0	11.4	12.4	15.9	2.19	24.3
8	.2	.2	2.8	3.0	1.0	1.0	8.2	9.2	16.9	1.21	19.5
9	.2	.2	2.7	2.9	7.3	1.8	10.4	12.2	9.2	5.23	56.2
10	.1	.3	2.0	2.3	2.1	.8	5.3	6.1	13.9	1.28	33.8
11	.1	.2	1.6	1.8	1.8	1.2	5.6	6.8	15.3	1.36	27.1
12	.0	.2	2.1	2.3	1.0	3.7	10.8	14.5	1.0	11.61	95.2
13	.0	.4	1.2	1.6	.4	1.2	2.1	3.3	20.8	.02	1.0
SET 2											
1	0.0	0.3	1.4	1.7	2.7	1.6	4.8	6.4	17.9	0.70	14.8
2	.1	.4	3.4	3.8	1.4	1.8	11.8	13.6	1.5	9.10	92.9
3	.1	.2	7.8	8.0	1.6	1.0	10.2	11.2	15.4	.85	26.7
4	.1	.1	1.5	1.6	.2	1.0	2.7	3.7	18.2	.28	13.3
5	.1	.2	1.7	1.9	3.8	1.0	7.7	8.7	18.3	.88	12.9
6	.0	.3	2.1	2.4	.4	.8	1.9	2.7	20.4	.01	2.9
7	.0	.3	5.2	5.5	1.6	.9	11.6	12.5	14.5	2.17	31.0
8	.0	.2	2.3	2.5	1.3	.8	8.5	9.3	16.5	1.45	21.4
9	.0	.4	2.7	3.1	6.8	1.9	9.0	10.9	11.7	3.46	44.3
10	.1	.2	2.2	2.4	2.6	.8	8.7	9.5	7.7	4.49	63.3
11	.1	.2	1.8	2.0	1.9	1.0	4.8	5.8	15.3	1.03	27.1
12	.1	.2	5.2	5.4	.9	2.0	12.2	14.2	1.3	8.25	93.8
13	.0	.2	2.0	2.2	.4	1.0	1.9	2.9	20.8	.01	1.0

Correlations

Results from previous aging tests in a metal bomb at 200° F (1) and from the current oven tests show that oxygen consumed and gum formed in the oven test can be used to predict storage performance for as long as 32 weeks at 110° F. All data needed to apply the method were obtained from analyses of fresh fuels and samples subjected to the 16-hour oven test. The correlation was developed from storage data reported in table 2 and oven test data reported in table 3 using the following mathematical relationships and data from the 16-hour oven test:

(1) Volume-percent oxygen that reacted during the oven test.

(2) A factor M_{16} obtainable from formulas derived from comparison of total gum determined on fresh gasolines, and after both 110° F storage (8, 16, 32, 44, and 52 weeks) and oven test (16 hours).

Volume-percent oxygen reacted and the factor MF_{16} were obtained by the following formulas:

$$(1)\quad \text{Percent } O_2 \text{ reacted} = \frac{\text{pct } O_0 - \text{pct } O_{16}}{\text{pct } O_0} \times 100,$$

$$(2)\quad MF_{16} = \frac{\text{pct } O_2 \text{ reacted}}{100} (\text{total gum}_{16} - \text{total gum}_0),$$

where percent O_0 is 21 percent oxygen in air in outage at start of the oven test,

percent O_{16} is the determined percent oxygen in air in the outage at end of the oven test,

total gum_{16} is the determined gum, soluble plus insoluble, at end of the oven test, mg/100 ml, and

total gum_0 is the determined gum, soluble plus insoluble, in the fresh fuel, mg/100 ml.

Average values for volume-percent oxygen reacted and MF_{16} from two sets of oven test data for 13 gasoline samples are included in table 4.

TABLE 4. - Average correlation factors from two sets of 200° F bottle oven tests

Gasoline	O_2 reacted, pct			MF_{16}			Inorganic residue, mg/100 ml		
	Set 1	Set 2	Avg	Set 1	Set 2	Avg	Set 1	Set 2	Avg
1	17.6	14.8	16.2	0.58	0.70	0.64	2.0	2.7	2.4
2	81.0	92.9	87.0	5.43	9.10	7.27	1.0	1.4	1.2
3	17.6	26.7	22.2	.46	.85	.66	1.6	1.6	1.6
4	15.2	13.3	14.3	.30	.28	.29	.3	.2	.3
5	18.6	12.9	15.6	.71	.88	.80	6.0	3.8	4.9
6	3.3	2.9	3.1	.07	.01	.04	.1	.4	.3
7	24.3	31.0	27.7	2.19	2.17	2.18	1.5	1.6	1.6
8	19.5	21.4	20.5	1.21	1.45	1.33	1.0	1.3	1.2
9	56.2	44.3	50.3	5.23	3.46	4.35	7.3	6.8	7.1
10	33.8	63.3	48.6	1.28	4.49	2.89	2.1	2.6	2.4
11	27.1	27.1	27.1	1.36	1.03	1.20	1.8	1.9	1.9
12	95.2	93.8	94.5	11.61	8.25	9.93	1.0	.9	1.0
13	1.0	1.0	1.0	.02	.01	.15	.4	.4	.4

The relationship between the average values for MF_{16} (table 4) and gum increase in 8 weeks storage at 110° F (table 2) is shown in figure 4.

It should be emphasized that the gum scale represents increase in total gum during this period. The relatively low amounts of gum increase predicted by this chart fit 12 of the 13 gasolines; exception, gasoline 9 was not used in the curve fitting. The equation of the line of regression (y) standard deviation of the observed data from the line of regression, s, and the coefficient of correlation for the relationship, r, are included on this and

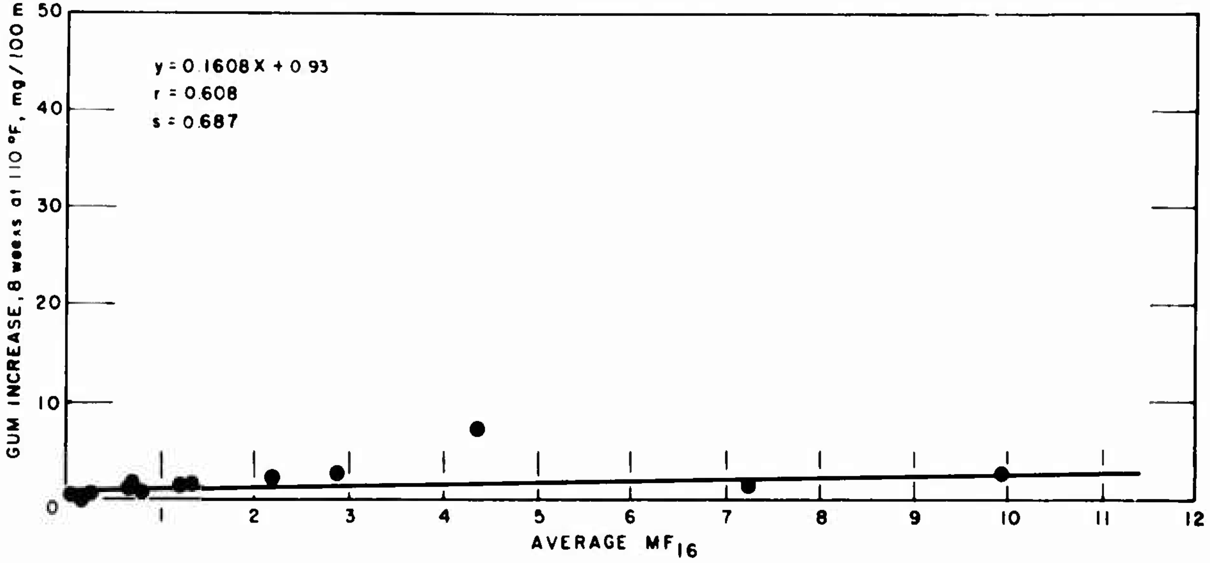

FIGURE 4. - Total Gum Increase in 8 Weeks of 110° F Storage Versus Average MF_{16}.

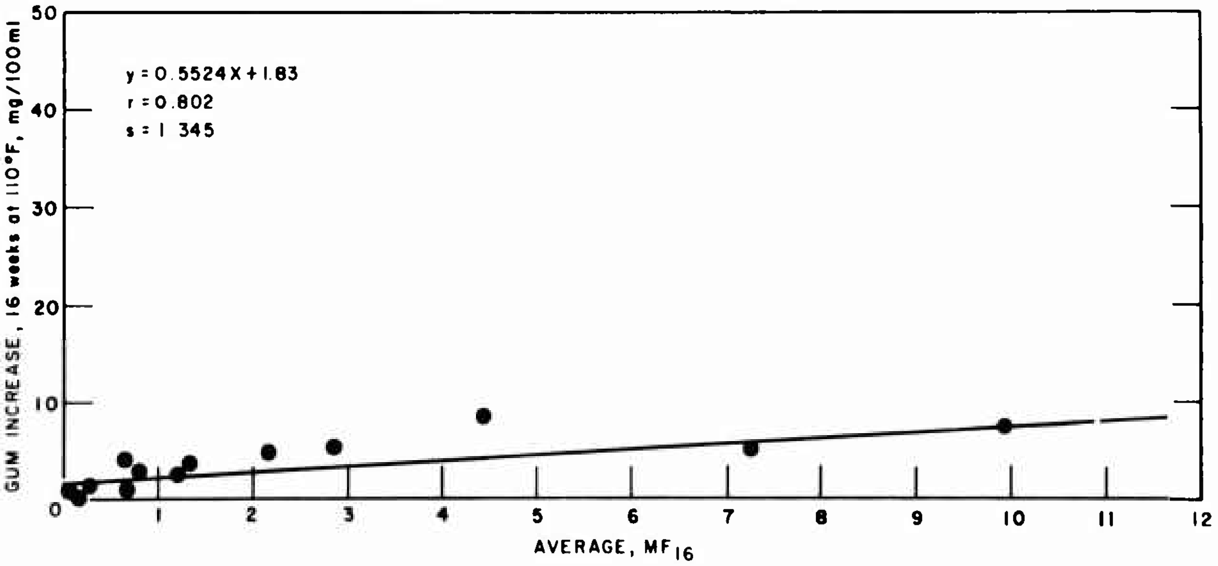

FIGURE 5. - Total Gum Increase in 16 Weeks of 110° F Storage Versus Average MF_{16}.

the following figures. All of the curves show a high coefficient of correlation.

A similar relationship, for increase in the gum during 16 weeks of storage at 110° F, to MF_{16}, is presented in figure 5. Again, gasoline 9 does not conform to the rest of the data.

Data from 32 weeks of 110° F storage showed the relationship plotted in figure 6. Good correlation is evident with the possible exception of gasolines 9 and 10.

After 44 weeks' storage at 110° F the relationship was checked by plotting in the same manner. Although a reasonable degree of correlation for most of the gasolines was noted through the 32-week, 110° F storage period, at 44 weeks of storage the MF_{16} relationship failed for data from about half the gasolines. Similar behavior of the 52-week storage data was found by a

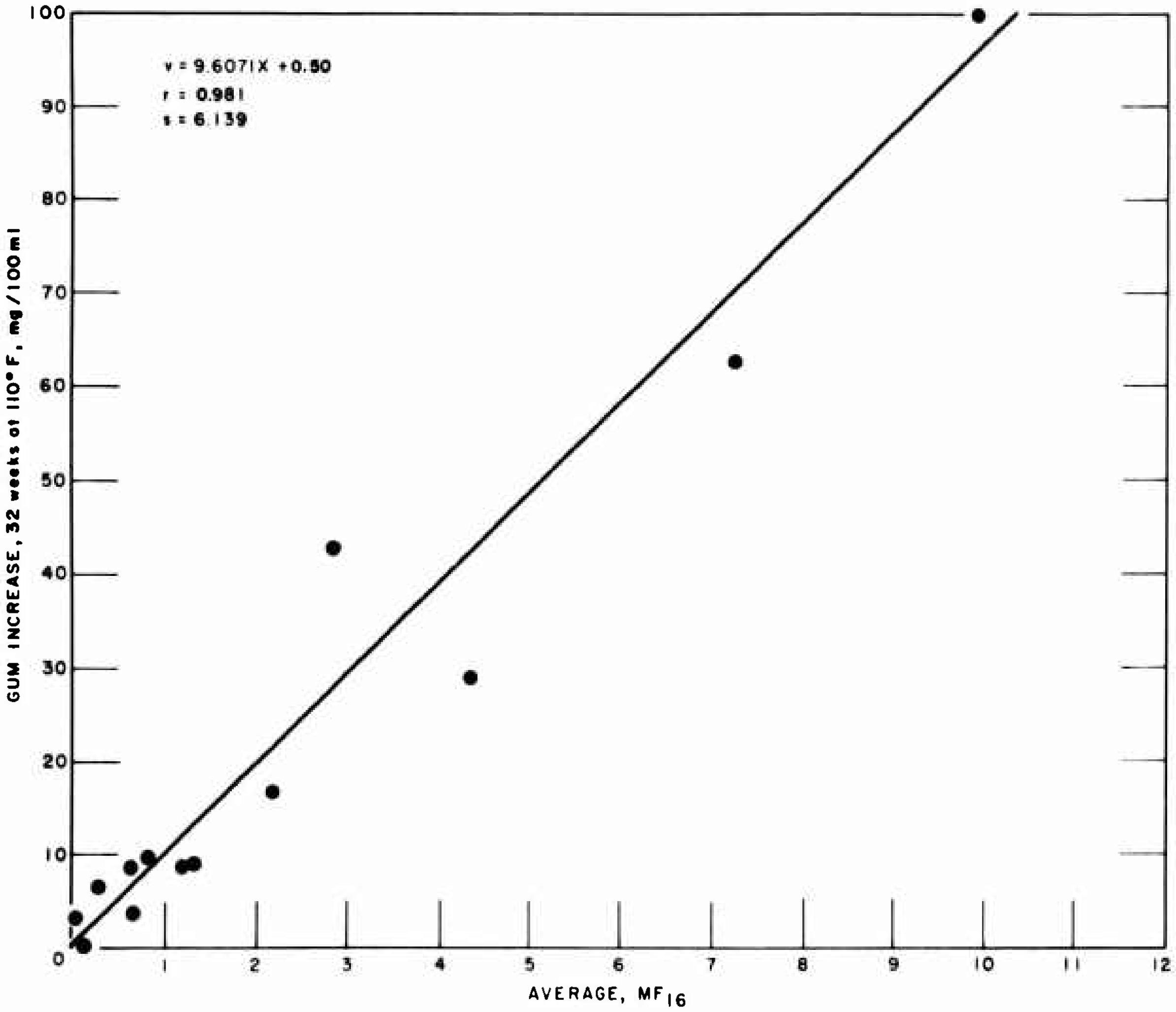

FIGURE 6. - Total Gum Increase in 32 Weeks of 110° F Storage Versus Average MF_{16}.

similar plot. The data showed that the MF_{16} correlation can be used to predict storage stability through 32 weeks of storage at 110° F, but that the correlation failed for longer periods of storage. Since 32 weeks of storage at 110° F is equivalent to about 5.7 years' storage at 80° F, it was assumed that stability prediction for 32 weeks of storage at 110° F was adequate to determine storage stability of gasolines, hence further correlation with 44- and 52-week data was not attempted.

In figure 7 the slopes of the gum-increase lines shown in figures 4, 5, and 6 were plotted on a logarithmic scale versus the time of storage on a linear scale. From this curve a coefficient for MF_{16} can be obtained for any storage time from 0 to 32 weeks of storage at 110° F. The average intercept value of the gum increase curves from figures 4, 5, and 6 was 1.1 mg/100 ml; this value was added to the MF_{16} factor when estimating gum formation.

From the relationship shown in figure 7 the following equations were developed for estimating gum formation at the stated interval of storage:

<u>8 Weeks at 110° F</u>

Total gum (mg/100 ml) = 0.15 MF_{16} + 1.1 + initial gum,

<u>16 Weeks at 110° F</u>

Total gum (mg/100 ml) = 0.60 MF_{16} + 1.1 + initial gum, and

<u>32 Weeks at 110° F</u>

Total gum (mg/100 ml) = 9.6 MF_{16} + 1.1 + initial gum.

In table 5 the results of calculating a predicted gum level are compared with determined gum values at 8, 16, and 32 weeks of 110° F storage for the group of gasolines. The same data are compared graphically in figure 8. Good correlation exists at the 0- to 10-mg level, as shown by the inset in this figure.

The deviations between predicted and each of the determined values of total gum were treated as paired values statistically (<u>6</u>), and no evidence of difference in the two sets of values was found. Comparison of standard deviations of total gum content calculated for duplicate bottles from storage, and standard deviations calculated for determined and predicted values, show essentially the same values at the 8-, 16-, and 32-week periods, which also indicates little difference between determined and predicted values. Thus the predicted values are, in most cases, as accurate as those obtained by determining gum formation in a single bottle of a fuel for as long as 32 weeks.

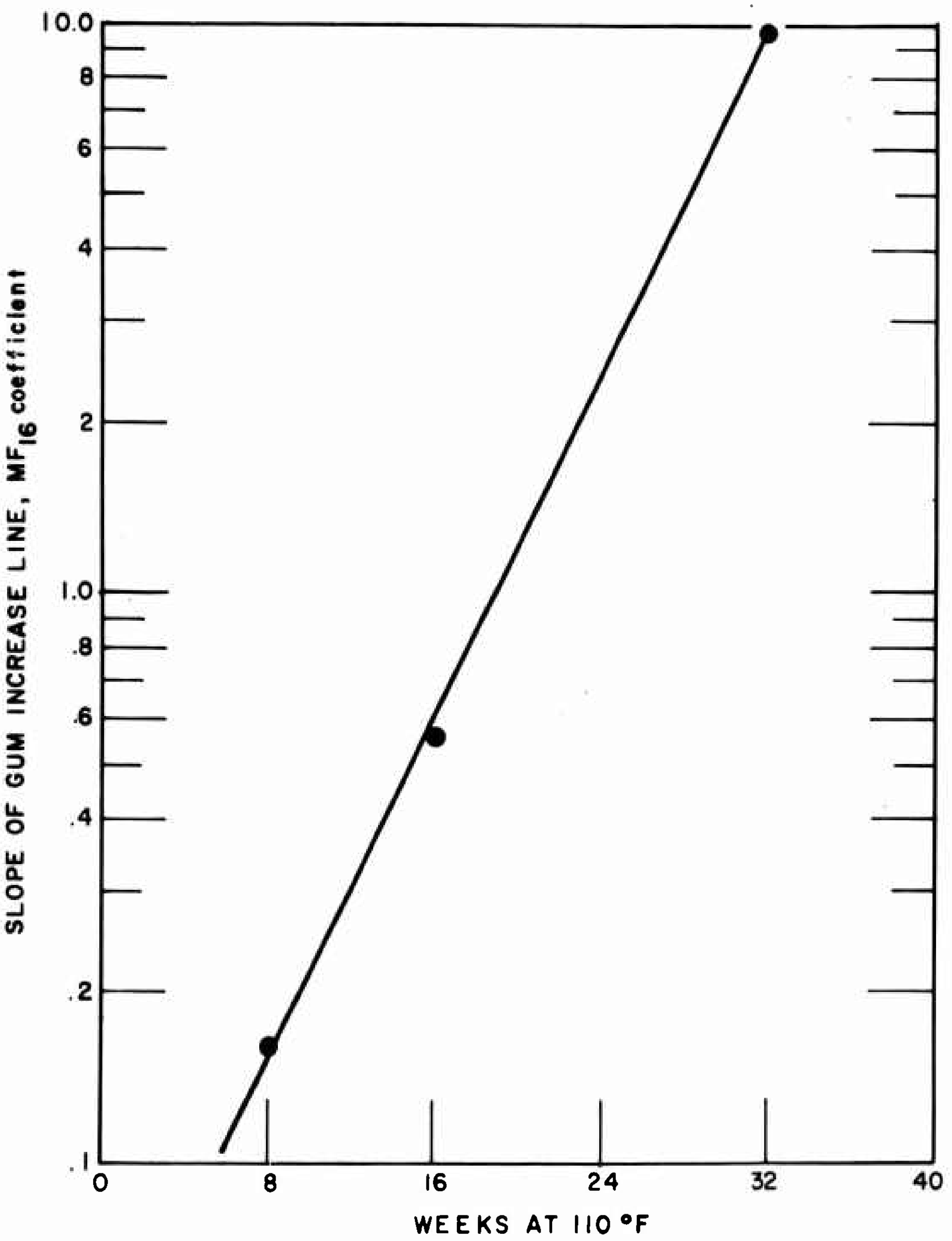

FIGURE 7. - Slope of Gum Increase Line Versus Weeks Stored at 110° F.

TABLE 5. - Gum formation--comparison of predicted and determined values for 110° F storage, mg/100 ml[1]

Gasoline	8 weeks' storage, gum = 0.15 MF_{16} + 1.1 + initial gum			16 weeks' storage, gum = 0.60 MF_{16} + 1.1 + initial gum			32 weeks' storage, gum = 9.60 MF_{16} + 1.1 + initial gum		
	Det[2]	Pred[3]	Dev[4]	Det[2]	Pred[3]	Dev[4]	Det[2]	Pred[3]	Dev[4]
1	2.7	2.9	-0.4	5.7	3.2	+2.5	10.1	8.9	+1.2
2	2.4	3.3	-.9	5.7	6.6	-.9	63.6	72.0	-8.4
3	8.9	8.9	.0	8.6	9.2	-.2	11.3	15.1	-3.8
4	2.0	2.4	-.4	2.6	2.6	.0	7.6	5.2	+2.4
5	3.1	3.2	-.1	4.9	3.9	+1.0	11.5	11.1	+.4
6	1.7	2.4	-.7	2.2	2.4	-.2	4.4	2.8	+1.6
7	5.6	4.8	+.8	8.1	5.8	+2.3	19.8	25.4	-5.6
8	4.4	4.3	+.1	6.6	4.9	+1.7	11.8	16.9	-5.1
9	10.0	4.7	+5.3	11.0	6.6	+4.4	31.8	45.8	-14.0
10	5.1	3.8	+1.3	7.3	5.1	+2.2	45.1	31.1	+14.0
11	3.0	3.1	-.1	4.0	3.6	+.4	10.2	14.4	-4.2
12	4.8	4.9	-.1	9.6	9.4	+.2	101.8	98.7	+3.1
13	1.7	2.7	-1.0	1.6	2.8	-1.2	2.3	4.1	-1.8

[1] Average of duplicate determinations.
[2] Determined.
[3] Predicted.
[4] Deviation.

Another correlation was developed to provide a method for estimating the inorganic residue that would be expected to form during 110° F storage. This correlation also requires only data obtained from the 16-hour oven test and mathematical relationships developed during this study.

The relationship between inorganic residue formed in 8 weeks, 110° F storage (table 2), and inorganic residue formed in the oven test (table 4) is shown in figure 9. The line is a least squares fit to the 8-week data with data from gasoline 5 omitted in fitting the line. Again, in the curves relating inorganic residue, the equation for the line of regression (y), the standard deviation of the points from the line (s), and the coefficient of correlation for the data (r) are included on the figures. Similar data for 16 weeks and 32 weeks are shown in figures 10 and 11, respectively.

Residue data from 44- and 52-week-storage periods became more erratic and after making similar plots for these data, correlation at the 44- and 52-week-storage periods was not pursued further.

In figure 12 the slopes of the lines in figures 9, 10, and 11 are plotted on a logarithmic scale versus the time of storage on a linear scale. This figure can be used for predicting inorganic residue in a manner similar to that used for predicting gum formation. The following equation is applicable for calculating inorganic residue that would be expected to form during storage from 0 to 32 weeks at 110° F:

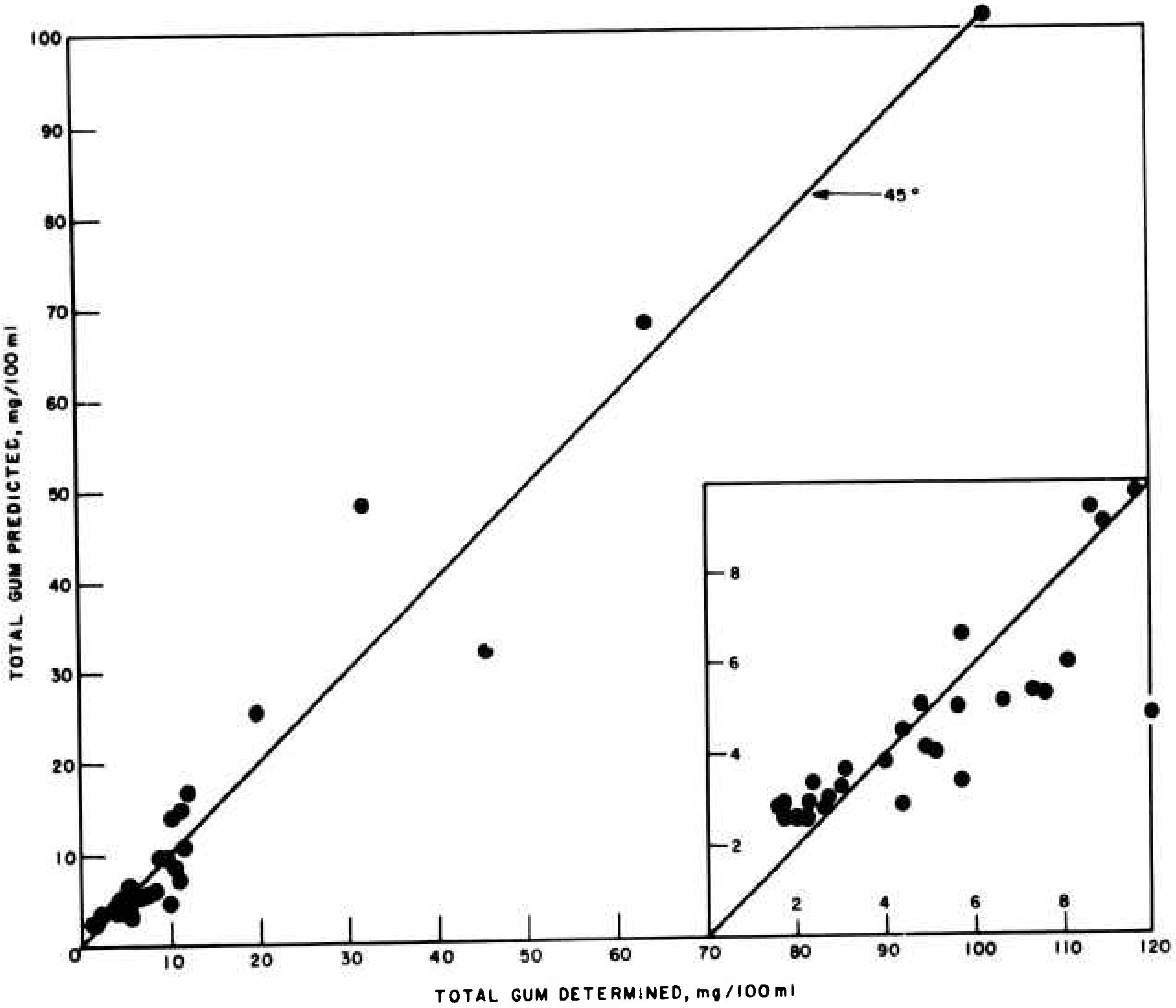

FIGURE 8. - Predicted and Determined Amounts of Total Gum, 13 Gasolines Stored for 8, 16, and 32 Weeks at 110° F.

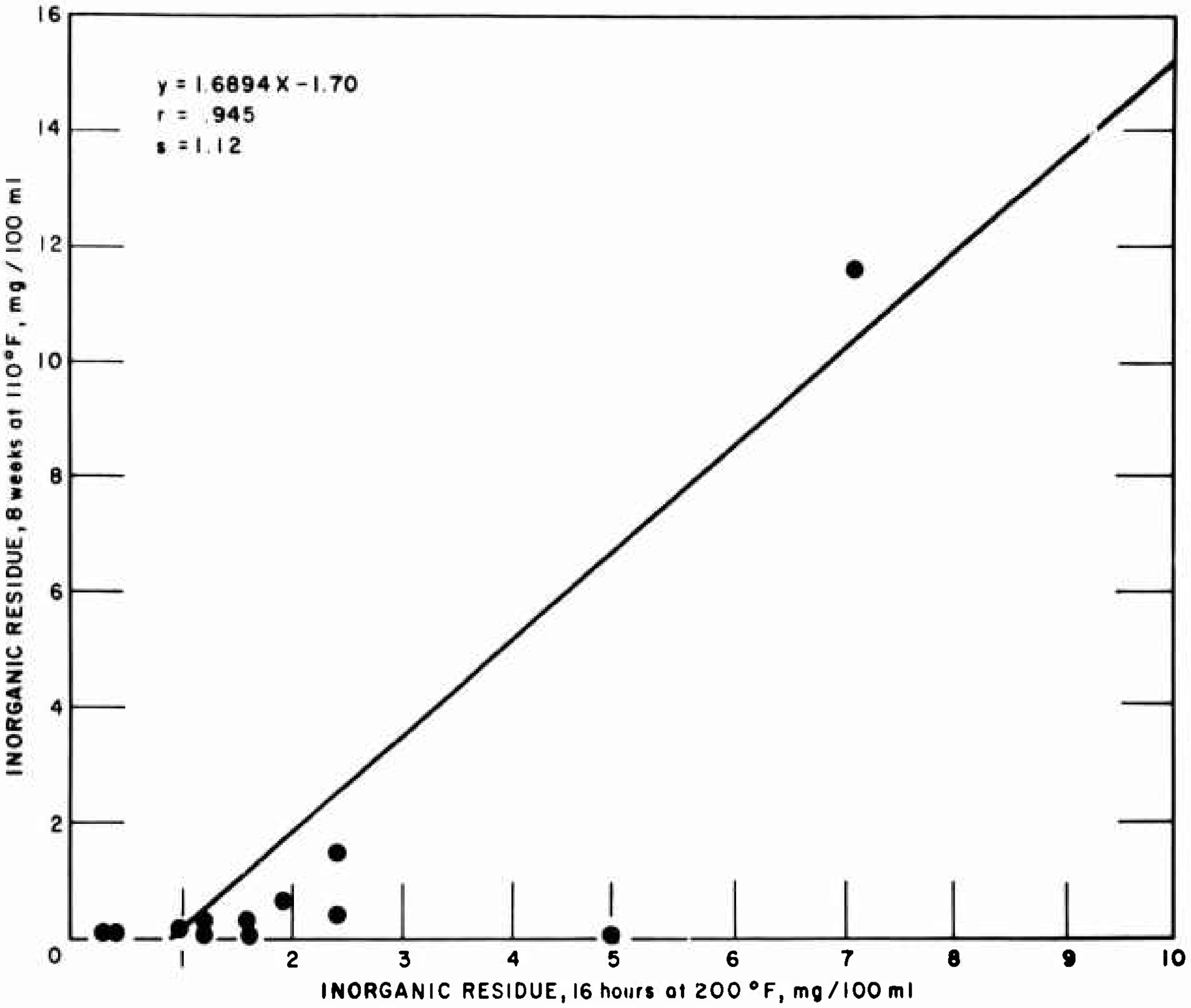

FIGURE 9. - Inorganic Residue Formed in 8 Weeks of 110° F Storage Versus Inorganic Residue Formed in 16-Hour 200° F Oven Test.

$$IR_{110} = m \times IR_{16} + C,$$

where IR_{110} is the calculated inorganic residue predicted for 110° F storage, mg/100 ml;

IR_{16} is the inorganic residue at end of the 16-hour oven test, mg/100 ml;

m is the slope obtained from figure 12; and

C is the average intercept obtained from figures 9, 10, and 11.

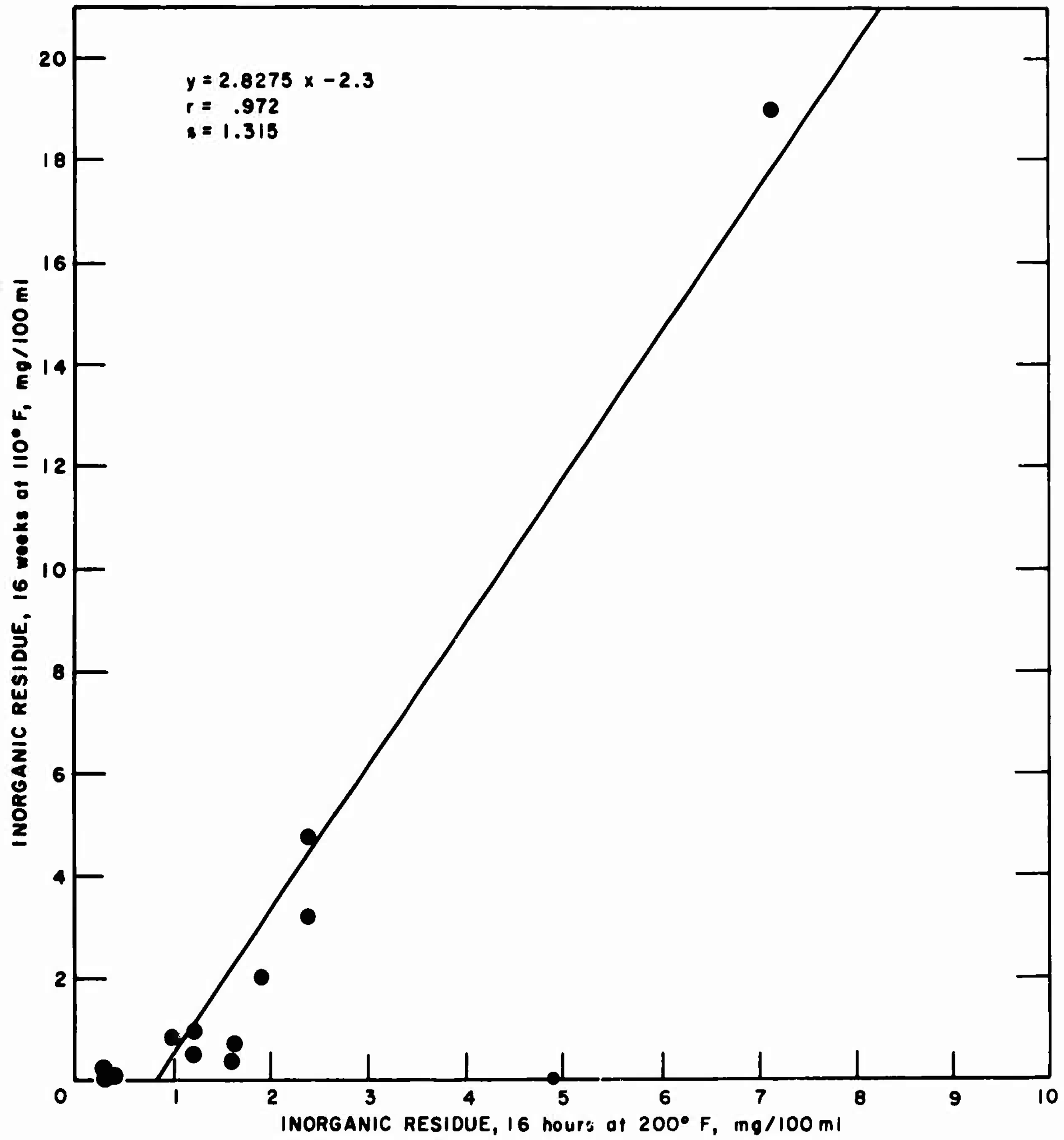

FIGURE 10. - Inorganic Residue Formed in 16 Weeks of 110° F Storage Versus Inorganic Residue Formed in 16-Hour 200° F Oven Test.

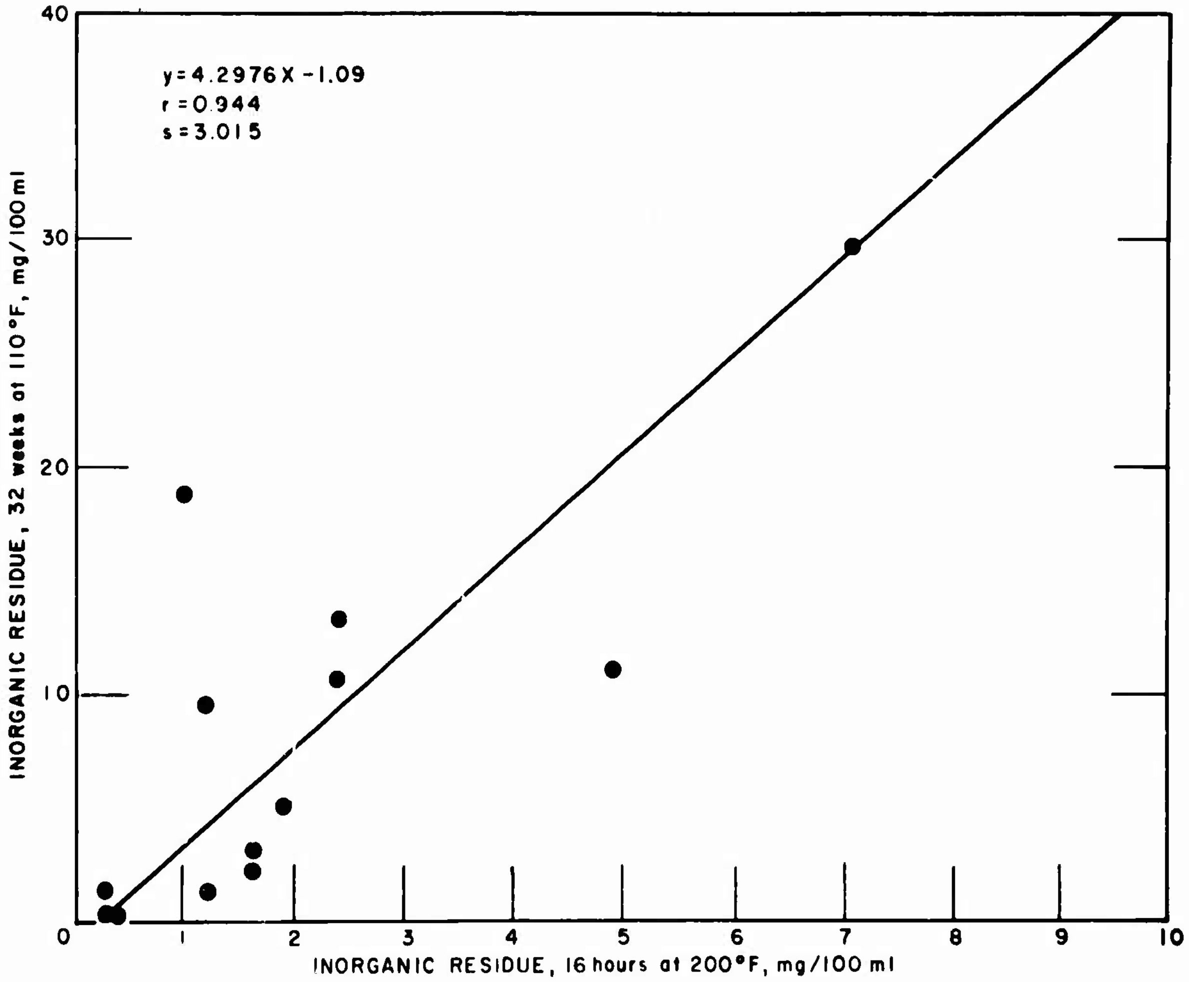

FIGURE 11. - Inorganic Residue Formed in 32 Weeks of 110° F Storage Versus Inorganic Residue Formed in 16-Hour 200° F Oven Test.

The following equations to predict the formation of inorganic residue during 110° F storage were derived from the preceding relationship:

Inorganic residue formation for 8 weeks at 110° F,

$IR_{110} = 1.9\ IR_{16} - 1.7$

Inorganic residue formation for 16 weeks at 110° F, and

$IR_{110} = 2.5\ IR_{16} - 1.7$

Inorganic residue formation for 32 weeks at 110° F.

$IR_{110} = 4.3\ IR_{16} - 1.7$

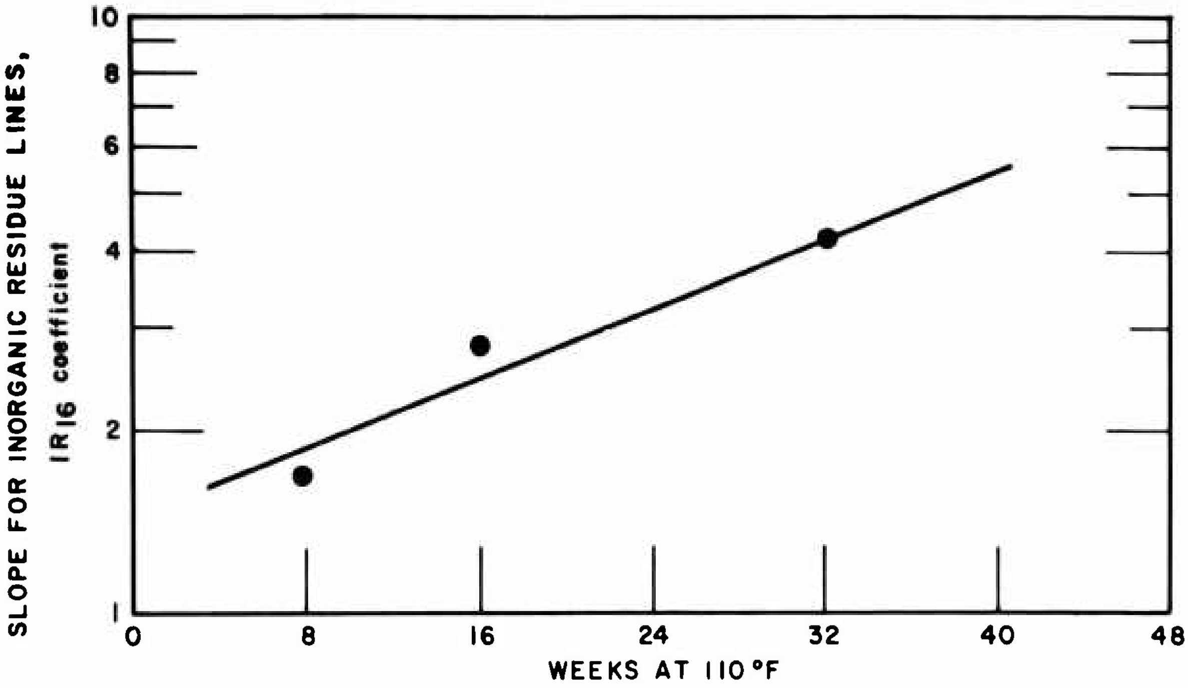

FIGURE 12. - Slope for Inorganic Residue Correlation Versus Weeks Stored at 110° F.

These equations were used to calculate predicted amounts of inorganic residue formation for the 13 gasolines for 8, 16, and 32 weeks' storage at 110° F. The predicted values are compared with determined values in table 6. The same comparison is made graphically in figure 13.

TABLE 6. - Comparison of predicted and determined inorganic residue formation in 13 gasolines during 110° F storage, mg/100 ml[1]

Gasoline	8 weeks' storage, $IR_{110} = 1.9\ IR_{16} - 1.7$			16 weeks' storage, $IR_{110} = 2.5\ IR_{16} - 1.7$			32 weeks' storage, $IR_{110} = 4.3\ IR_{16} - 1.7$		
	Det[2]	Pred[3]	Dev[4]	Det[2]	Pred[3]	Dev[4]	Det[2]	Pred[3]	Dev[4]
1	0.5	2.9	-2.4	4.8	4.3	+0.5	10.7	8.6	+2.1
2	.4	.6	-.2	1.0	1.3	-.3	9.5	3.5	+6.0
3	.1	1.3	-1.2	.4	2.3	-1.9	3.0	5.2	-2.2
4	.1	.0	+.1	.2	.0	+.2	1.4	.0	+1.4
5	.0	7.6	-7.6	.4	10.6	-10.2	11.0	19.4	-8.4
6	.1	.0	+.1	.1	.0	+.1	.2	.0	+.2
7	.3	1.3	-1.0	.7	2.3	-1.6	2.3	5.2	-2.9
8	.1	.6	-.5	.5	1.3	-.8	1.2	3.5	-2.3
9	11.6	11.8	-.2	19.0	16.1	+2.9	29.1	28.8	+.3
10	1.5	2.9	-1.4	3.2	4.3	-1.1	13.2	8.6	+4.6
11	.7	1.9	-1.2	2.0	3.1	-1.1	5.0	6.5	-1.5
12	.2	.2	.0	.9	.8	+.1	18.8	2.6	+16.2
13	.1	.0	+.1	.1	.0	+.1	.1	.0	+.1

[1] Determined values are averages of duplicate determinations.

[2] Determined.

[3] Predicted.

[4] Deviation.

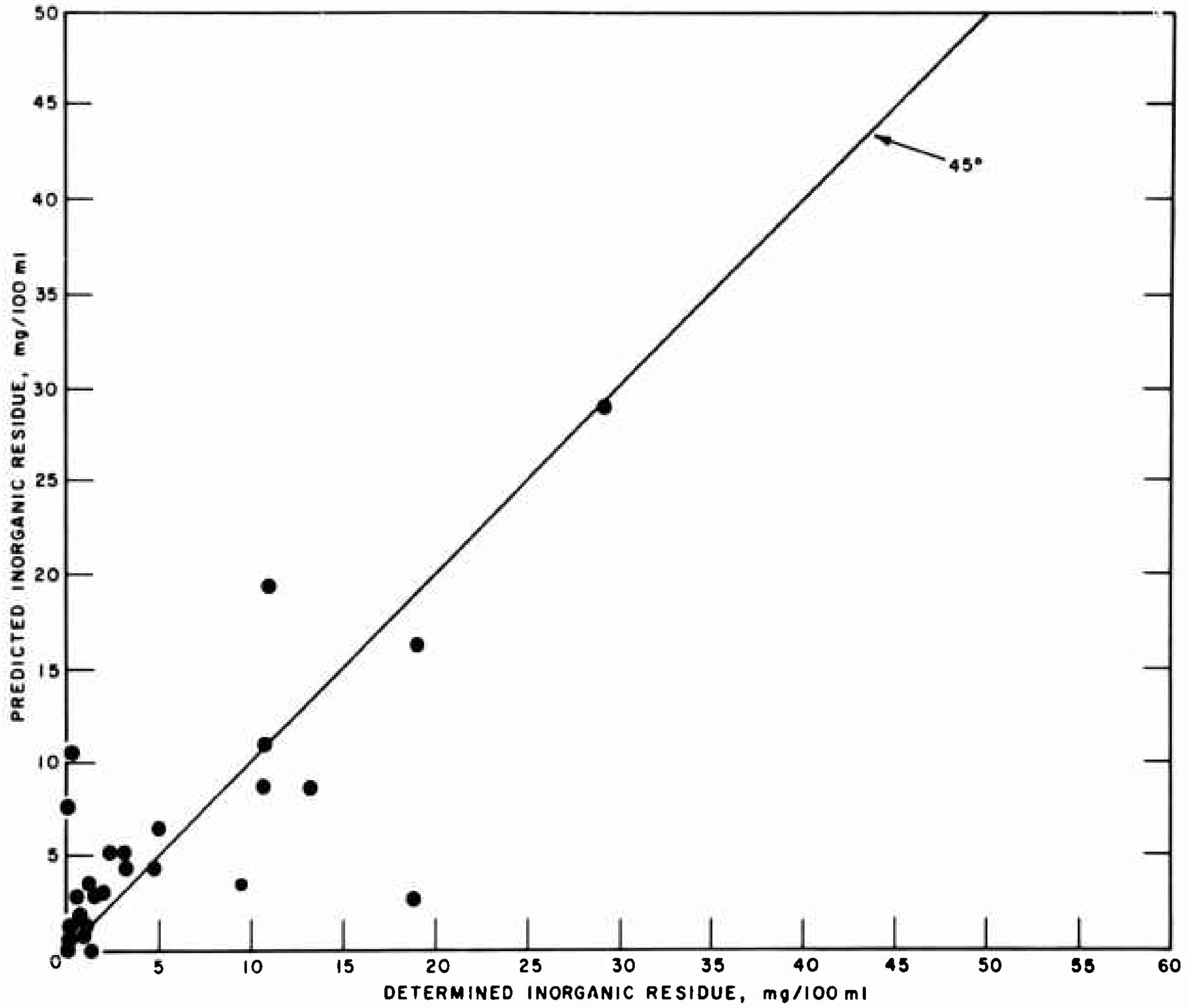

FIGURE 13. - Predicted and Determined Amounts of Inorganic Residue, 13 Gasolines Stored 8, 16, and 32 Weeks at 110° F.

A statistical test for differences in sets of data (6) showed no evidence of difference in inorganic residue in the sets of data from two types of bottles, thus justifying the use of averages from the two sets. Similar testing of determined and predicted values of inorganic residue for 8, 16, and 32 weeks' storage indicated that values from the correlations were essentially as reliable as the average determined values.

CONCLUSIONS

A 16-hour gasoline stability test was developed that can be used to predict the amounts of gum and inorganic residue that will form in a leaded gasoline stored at 110° F for any period up to 32 weeks. Comparison of predicted and determined values of gum and inorganic residue formed in 13 gasolines stored at 110° F for 8, 16, and 32 weeks indicated that the predicted values were as reliable as determined values. By use of a modification of the

Arrhenius equation (8) the 110° F storage data can be used to estimate gasoline storage stability at lower temperatures. Since 32 weeks' storage at 110° F is equivalent to over 5 years' storage at 80° F, the prediction method presented was judged to be adequate for any practical storage of motor gasoline.

ACKNOWLEDGMENTS

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[6] Titles enclosed in parentheses are translations from the language in which the items were published.

APPENDIX A.--110° F STORAGE TEST OF GASOLINE STABILITY

Cleaning Storage Bottles

Add chromic acid cleaning solution to the bottle, swirl, and roll the bottle as solution is poured to next bottle to insure complete contact of acid with entire inner surface;

Invert bottle over a stream of tap water and flush for one minute;

Rinse with a 25:75 solution of concentrated ammonium hydroxide solution in water for ½ minute;

Allow the bottle to drain. Place in an inverted position in an oven and dry overnight at 150° C.

Aging at 110° F

Filter the fuel through a GA-6 Metricel[1] 0.45-micron pore size filter to remove particles. Place 350 ml of each fuel in each of twelve 40-ounce (1,180 ml), crown-and-cap, amber bottles. Seal with crimp caps using Teflon liners. Store in the dark in a constant-temperature room at 110° F. After each storage interval--8, 16, 32, and 52 weeks from the beginning of storage--remove two samples of every gasoline 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

(Adapted From Du Pont Petroleum Laboratory Method No. G34-52)

Remove the sample from 110° F storage and place in the cold room.

When the sample has cooled to 35° to 40° F, sweep the interior of the 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.

Recap the sample and when the sample has warmed to room temperature, return it to 110° F storage.

Analyzing Storage Samples

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

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

D381 (2, pp. 166-172).[2] Insoluble gum is dissolved in organic solvents and weighed after evaporation of solvent. Inorganic residue is determined by differential weighing of the crucible.

Materials

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

Size 9 neoprene stopper, bored to accept delivery tube.

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

Crucible holder.

ASTM D381 air-jet gum beakers; eight needed.

Graduated bottles, at least 12-ounce; two needed.

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.

Procedure

Soluble Gum.--Weigh a filtering crucible (hereinafter called "filter") and eight gum beakers. Assemble the reservoir-stopper-filter-holder arrangement for filtration as shown in figure 1. With 1- to 5-psi air pressure, pass the aged fuel from bottle A through the filter and collect the filtrate in a graduated bottle. Set aside. Pass the contents of 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 soluble gum on each. Report their average as soluble gum, mg/100 ml.

Insoluble Gum.--Place a container beneath the filter. Rinse each storage bottle and the filter free of fuel by three successive 50-ml portions of heptane with gentle 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.

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[2] Underlined numbers in parentheses refer to items in the list of references preceding the appendixes.

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 same filter and carry out the gum solvent steps on bottle B.

Evaporate solvent from the two solutions using ASTM Method D381.

$$\text{Insoluble gum, mg/100 ml} = \frac{\text{mgA} + \text{mgB}}{7} .$$

Inorganic Residue.--To determine the residue collected on the filter, dry the filter in a 200° F oven for 1 hour, cool in a desiccator without desiccant for at least 2 hours, and weigh.

$$\text{Inorganic residue, mg/100 ml} = \frac{\text{mg residue}}{7} .$$

To calculate total gum add the insoluble gum to the soluble gum value.

APPENDIX B.--RAPID STABILITY TEST AT 200° F USING BEVERAGE BOTTLES

Cleaning the Beverage Bottles

Scrub with a detergent solution, and rinse with water;

Add chromic acid cleaning solution to the bottle, swirl, and roll the bottle to insure complete contact of acid with entire inner surface;

Rinse with tapwater, then invert the bottle and flush with a stream of distilled water;

Allow the bottle to drain. Dry overnight in a 300° F oven.

Aging at 200° F

Filter the fuel through a GA-6 Metricel 0.45-micron pore size filter to remove particles. Place 130 ml of fuel in each of two 16-ounce beverage bottles at room temperature. Seal the bottles with special crimp-type caps lined with Teflon and 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, 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.

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 (2, pp. 166-172). Insoluble gum is dissolved in gum solvent and measured by evaporation of solvent. Inorganic residue is determined by weighing the filter.

Materials

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

Size 9 neoprene stopper, bored to accept delivery tube.

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

Crucible holder.

ASTM D381 air-jet gum beakers; eight needed.

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.

Procedure

Soluble Gum.--Weigh a filtering crucible (hereinafter 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.

Insoluble Gum.--Place a container beneath the filter. Rinse each bottle and the filter free from fuel by three successive 50-ml portions of heptane with gentle 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 same filter and carry out the gum solvent steps on bottle B.

Evaporate solvent from the two solutions using ASTM Method D381.

$$\text{Insoluble gum, mg/100 ml} = \frac{\text{mgA} + \text{mgB}}{2.6} .$$

Inorganic Residue.--To determine the residue collected on the filter, dry the filter in a 200° F oven for one hour, cool in a desiccator without desiccant at least 2 hours, and weigh.

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

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

APPENDIX C.--METHOD FOR OXYGEN IN OUTAGE OF TEST BOTTLES

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

Conditions

Gas chromatograph equipped with hot-wire detector; 5-foot by ¼-inch copper column; 30- to 60-mesh Molecular Sieve 13X, conditioned at 400° to 600° F for 6 hours with helium; ambient temperature; helium flow 67 ml/min; filament current 180 milliamperes.

Procedure

Inject an amount of the sample of outage to produce a nearly full-scale nitrogen peak (60 to 80 microliters). Repeat once or twice to get a duplicate pattern. Inject an amount of air to give a similar nitrogen peak.

Calculations

Since the chromatographic column does not resolve 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. The following procedure is used for calculation.

1. Correct the oxygen peak height on the air sample for argon.

2. Divide this corrected peak height by the height of the nitrogen peak (R_a).

3. Obtain these ratios from an average of the three or four air measurements associated with a sample.

4. Obtain the oxygen/nitrogen ratio for the replicate sample injections (R_s) in a similar manner.

Based upon the assumption that the ratio of oxygen to nitrogen will stay constant unless the oxygen is depleted, the following formula may be applied to the average ratios obtained:

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

where R_a = oxygen/nitrogen peak heights from air.

R_s = oxygen/nitrogen peak heights from sample.

3.71748 = ratio of volume percent nitrogen to volume-percent oxygen in air.

To calculate percent oxygen in air in outage on a whole sample basis the above result should be reduced by 1 percent of the determined oxygen level.