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EVALUATION OF MOTOR GASOLINE STABILITY

INTERIM REPORT
BFLRF No. 266

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19. ABSTRACT

specification stability test. Based upon the data generated under the four phases of this storage stability program including supporting data obtained from literature sources and current surveillance information on both military and industry practices, the method recommended for evaluating stability of commercial/military motor gasoline (procured for long-term storage) is the ASTM D 873 Method using a 6-hour aging existent gum maximum limit of 5 mg/100 mL. The ability of this test to distinguish between stable and unstable low induction period fuels and/or components is discussed. In evaluating the individual potential gasoline components, a pyrolysis naphtha was shown to be generally an order of magnitude less stable than all other streams, and coker naphtha was shown to possess poor stability characteristics. LCC and HCC naphthas, which make up the bulk of unleaded gasoline, have lower stability than the remaining components.

In addition to determining the viability of 360-minute induction period in F-57 fuel as a substitute for or replacement of 480-minute (F-46) criteria, and as an extension of work directed toward predicting stability characteristics of gasolines, gum preventive compounds and the methodology of MIL-G-53042 are examined as a portion of the current project.

More specifically, gasoline and gasoline components were tested by various ASTM test methods including D 525, D 873, D 381, and FTM 500.1. The gasoline and gasoline components were monitored for selected properties during storage at 43°C, 54°C, and ambient conditions in an effort to relate accelerated properties by D 525 and D 873 to properties observed during storage at various temperatures, all of which are higher than storage underground [estimated at around 67°F (19°C)] or above-ground tank storage [estimated at 86°F (30°C)]. The Central European Pipeline System uses buried (cut and cover) tanks that maintain product temperatures fairly stable throughout the year at approximately 10° ± 6°C.

Accomplishments: The results completed to date have demonstrated the proposed storage stability test, a modification of ASTM D 873, to be acceptable in predicting motor gasoline stability. This method has been shown to correlate with both unwashed and existent gum formations of gasolines stored up to 4 years under ambient shaded storage in San Antonio, TX. Based on the data generated (under the four phases of this storage stability program, including supporting data obtained from literature sources and current surveillance information on both military and industry practices), the method recommended to be adopted for evaluating stability of commercial/military motor gasoline will consist of the modified ASTM D 873 method using a 6-hour aging existent gum maximum limit of 5 mg/100 mL. Selection of this limit for D 873, 6-hour test, was shown to expect the ambient storage samples to remain below a D 381 gum value of 5 mg/100 mL in ambient storage. Additionally, if the existent gum storage value is to be limited to 4 mg/100 mL, then the ASTM D 873, 6-hour, gum value may need to be limited to an increase of 5 mg/100 mL above the initial gum level.

The 5 mg/100 mL D 873 (6-hour) limit represents a compromise in predicting storage stability for a 4-year period for military gasolines; i.e., F-46 gasolines have been required to meet both an ASTM D 525 limit of 480 minutes minimum and an ASTM D 381 unwashed gum limit of 4 mg/100 mL maximum.

It is recommended as a minimum that new commercial/military gasoline be required to meet both the modified ASTM D 873 existent gum limit of 5 mg/100 mL maximum after a 6-hour aging period and the ASTM D 381 existent gum limit of 4 mg/100 mL maximum.

Military Impact: Methodology developed in this program provides the U.S. military with additional capability to prevent deterioration of stored gasoline important to combat readiness of gasoline-utilizing equipment and the costly requirement of premature turnover of stored stocks.

EXECUTIVE SUMMARY

Problems and Objectives: This project began because of a pending change from a military combat gasoline (F-46) to a new commercial/military gasoline (F-57), which is exchanged among the North Atlantic Treaty Organization (NATO) member nations. The existing and proposed specifications differ with respect to oxidation stability and required antioxidant content. MIL-G-3056 (Combat Gasoline), F-46, calls for a minimum induction period of 480 minutes (ASTM D 525) and requires antioxidant at 14 to 43 grams per cubic meter (5 to 15 lb/1000 bbl) and metal deactivator at 2.8 to 8.6 grams per cubic meter (1 to 3 lb/1000 bbl) of gasoline. F-57, commercial/military gasoline, specifies a 360-minute minimum induction period with antioxidant not required. The project was initiated in order to understand the difference between 360- and 480-minute induction period (vis-a-vis required storage stability of gasoline stocks already owned as well as future stocks required), and to provide a data base for support of U.S. position on F-57 specification limits prior to the 1989 promulgation date for F-57.

Material procured under Specification MIL-G-3056 has historically tested in excess of 1440-minute induction period. A 1983 survey of military gasolines interchanged under the NATO F-46 military combat gasoline showed that some gasolines were of inferior stability. The survey raised the possibilities that the quality of gasolines placed in storage in the Central European Pipeline System may be changing and/or that the stringent existing criteria are inadequate.

The incentive for the project, then, is to protect an investment in current stocks, to provide for a variable quality in future fuels, and, at the same time, to consider changes in the fuel standardization policy represented by adoption of the proposed F-57 specification.

The objectives of this program were to develop an improved method for predicting long-term (up to 4 years) storage stability of automotive gasolines and to evaluate the stability characteristics of gasolines having induction periods (ASTM D 525) near 360 minutes. It was also desired to determine if gasoline gum preventive compounds (as defined in MIL-G-53042) are effective in improving the storage stability of gasolines having induction periods at or below 480 minutes.

Importance of Project: The ability to protect stored gasoline stocks from being contaminated with poor stability gasoline and to guarantee good stability quality of stored gasoline to prevent the need for premature turnover of stocks will provide security and maintenance cost avoidance. Prevention of vehicle and small unit storage degradation of fuel will guarantee trouble-free operation on nongumming gasoline and maintenance cost avoidance.

Technical Approach: U.S. Army Belvoir Research, Development and Engineering Center was requested to initiate a series of accelerated and static stability tests on various gasolines to develop a technical basis for future United States action. Since no NATO nation or the U.S. petroleum industry could supply data by which gasolines possessing 360-minute minimum induction periods may be evaluated and the guidelines for the NATO F-46 had evolved from MIL-G-3056, the project was started at the U.S. Army Belvoir Fuels and Lubricants Research Facility (BFLRF) at Southwest Research Institute (SwRI) in San Antonio, TX.

FOREWORD/ACKNOWLEDGMENTS

This work was performed by the Belvoir Fuels and Lubricants Research Facility (BFLRF) located at Southwest Research Institute (SwRI), San Antonio, TX, during the period October 1984 to September 1990 under Contract No. DAAK70-87-C-0043 with the U.S. Army Belvoir Research, Development and Engineering Center. Mr. T.C. Bowen of Belvoir RDE Center (STRBE-VF) served as the contracting officer's representative, and Mr. M.E. LePera, chief of Fuels and Lubricants Research Division (STRBE-VF), served as the project technical monitor.

The authors acknowledge the technical assistance provided by Southwest Research Institute personnel in conducting this work. Ms. Lona McInnis maintained the data base over the course of this 5-year plus project. The authors also acknowledge the editorial assistance provided by Mr. J.W. Pryor, and Mses. E.F. Cantu and L.A. Pierce in the preparation of this report.

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I. INTRODUCTION

Efforts are being made by North Atlantic Treaty Organization (NATO) nations to adopt NATO Code No. F-57 (commercial low lead gasoline) as a replacement for NATO Code No. F-46 (military gasoline) under which the United States provides MIL-G-3056 (1)* product. The NATO Code Nos. and U.S. Military Specifications that pertain to this program are detailed in TABLE 1.

TABLE 1. Selected Stability-Related Parameters for NATO Code and U.S. Military Specification Gasolines

Code or Specification	NATO F-46	NATO F-57	MIL-G-3056
Gasoline Type	Military	Commercial	Military
ASTM D 525 Induction Period, minutes, min.	480	360	480
ASTM D 381 Unwashed Gum, mg/100 mL, max.	4	--	4
Existent Gum, mg/100 mL, max.	--	4	--
Corrosion Inhibitors	Required	Optional	Optional
Oxidation Inhibitors	Optional	Optional	Required
Metal Deactivators	Optional	Optional	Required

The change from F-46 to F-57 is being driven by a number of factors, including maximal use of commercially available fuels, simplification of fuel procurement, and increased flexibility in maintaining war reserve requirements. However, with respect to the stability issue, one principal difference of major concern between current F-46 and the proposed F-57 requirements is the ASTM D 525 (2) induction period requirement.

> (Note: The *induction period* is defined as the time elapsed between placing of the sample bomb in the bath and the break point at 100°C. *Break point* is defined as the point in the pressure-time curve that is preceded by a pressure drop of exactly 2 psi (13.8 kPa) within 15 minutes and succeeded by a drop of not less than 2 psi in 15 minutes.)

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* Underscored numbers in parentheses refer to the list of references at the end of this report.

F-46 calls for 480 minutes minimum induction period, whereas F-57 specifies a 360-minute minimum. A second difference associated with this stability issue is the requirement for addition of antioxidant at 14 to 43 grams per cubic meter (5 to 15 lb/1000 bbl) and metal deactivator at 2.8 to 8.6 grams per cubic meter (1 to 3 lb/1000 bbl) in MIL-G-3056 but not in either F-46 or F-57 (which allow but do not require antioxidant or metal deactivator). It is necessary that the United States protect gasoline stocks previously procured in compliance with MIL-G-3056 from contamination with inferior product. Additionally, it is desired to prevent inferior gasoline from being placed in vehicles and small storage containers that are exposed to more severe deterioration conditions of heating, temperature cycling, and breathing.

A survey of MIL-G-3056 gasolines available at military installations in the United States was conducted during the 1950's.(3) The bulk of these gasolines had induction periods in excess of 1440 minutes. Commercial gasoline specification ASTM D 439 (superseded by ASTM D 4814) allows commercial gasoline (not intended for long-term storage) to have induction periods as low as 240 minutes.

Surveillance data were previously presented from the Central European Operating Agency (CEOA) and summarized in Appendix A, which demonstrated that a gum specification for procurement was inadequate protection against fuel instability.(4)

By suitable modification to ASTM D 873, it may be possible to combine features of D 525 and D 381 to accomplish what either test alone cannot; i.e., an accelerated test whose results can ensure a (satisfactorily) stable gasoline. A program was designed and subsequently initiated within the United States to provide the necessary data for accomplishing these objectives. The program was designed to determine:

1. Viability of ASTM D 873, slightly modified, as a means to accurately assess the long-term storage stability of motor gasolines (i.e., up to 4 years), and

2. Stability characteristics and engine-depositing tendencies of gasoline possessing ASTM D 525 induction periods in the range of 360 minutes.

II. BACKGROUND

At the U.S. Army's request, the Coordinating Research Council (CRC) conducted three desert storage tests on motor and aviation gasoline during 1943-1945. The findings in that work (5) indicated that gasoline stability could be evaluated using ASTM tests for induction period (D 525) and oxidation stability (D 873). Also, it was determined that 480 minutes represented a realistic minimum induction period specification for commercial gasolines of that era, and that an acceptable correlation existed between results obtained via laboratory storage at 43°C and desert storage results. The 480-minute induction period was to reflect a 4-year storage requirement for "combat gasolines" compared to typical "commercial gasolines" that did not have long-storage time requirements and had 240-minute minimum induction period specifications. The work employed a "5-hour aging gum test" and 6 months as the predictable storage period (at 43°C).

In another CRC program conducted in 1944 and 1945 in Texas and California (6), gasolines with gum levels of 1.5, 7, 10, 25, and 50 mg/100 mL were used in several vehicles for up to 500 hours of operation. Results showed that most of the vehicles operating with gasolines having 7 mg/100 mL gum (or more) failed after relatively few hours of operation. Such failures were due to excessive intake valve manifold and port deposits.

Work conducted at the U.S. Bureau of Mines, Bartlesville, OK, resulted in the development of a 16-hour "oven test" at 95°C (203°F). Test results were correlated with 43°C storage for various periods of time and were used in a monograph relating time at 43°C and multiplication factor at 95°C (16 hour) to reach designated gum level.(7) This procedure was never generally accepted by industry primarily due to poor gum data precision, although some techniques for analyzing stored samples have been adopted from this work.

Schrepfer and Stansky of UOP, Inc. (formerly Universal Oil Production) utilized a "4-hour accelerated gum" test at 100°C.(8) Results of this test were correlated with results after 3-month darkroom storage at 43°C. This correlation suggests that the "4-hour accelerated gum" data, along with field and laboratory experience, allow one to reliably predict the rate of gum formation at 43°C (for 3 months) and, therefore, at ambient (29°C) storage for 1 year. The prediction was reduced to an "if then" statement, which was "if 4-hour accelerated gum is <5 mg/100 mL, then gasoline gum will be <3 mg/100 mL in dark storage at 43°C, which means in storage of 1 year at ambient, gasoline gum will be <3 mg/100 mL. The "4-hour accelerated gum" test is a modification of ASTM D 873 and is essentially the method adopted for the work reported here.

The data of Schrepfer and Stansky were originally presented in graphical form and have now been digitized for verification through statistical analysis. Fig. 1 presents the result in graphic form. The findings reinforce the conclusion that D 525 induction period is a poor predictor of stability. Fig. 2 recreates these data over the range of induction periods of the most interest for this program. A coefficient of determination of 0.003 (by linear regression) was obtained. Correlation results of the modified D 873 test with gum after 3-month dark storage at 110°F (43°C), shown in Fig. 3, convey a coefficient of correlation of 0.26. However, Schrepfer and Stansky make the interesting observation from Fig. 3 that 98 percent of the samples that result in a 4-hour gum of 5.0 mg/100 mL (or less) generate less than 3.0 mg/100 mL in the 3-month

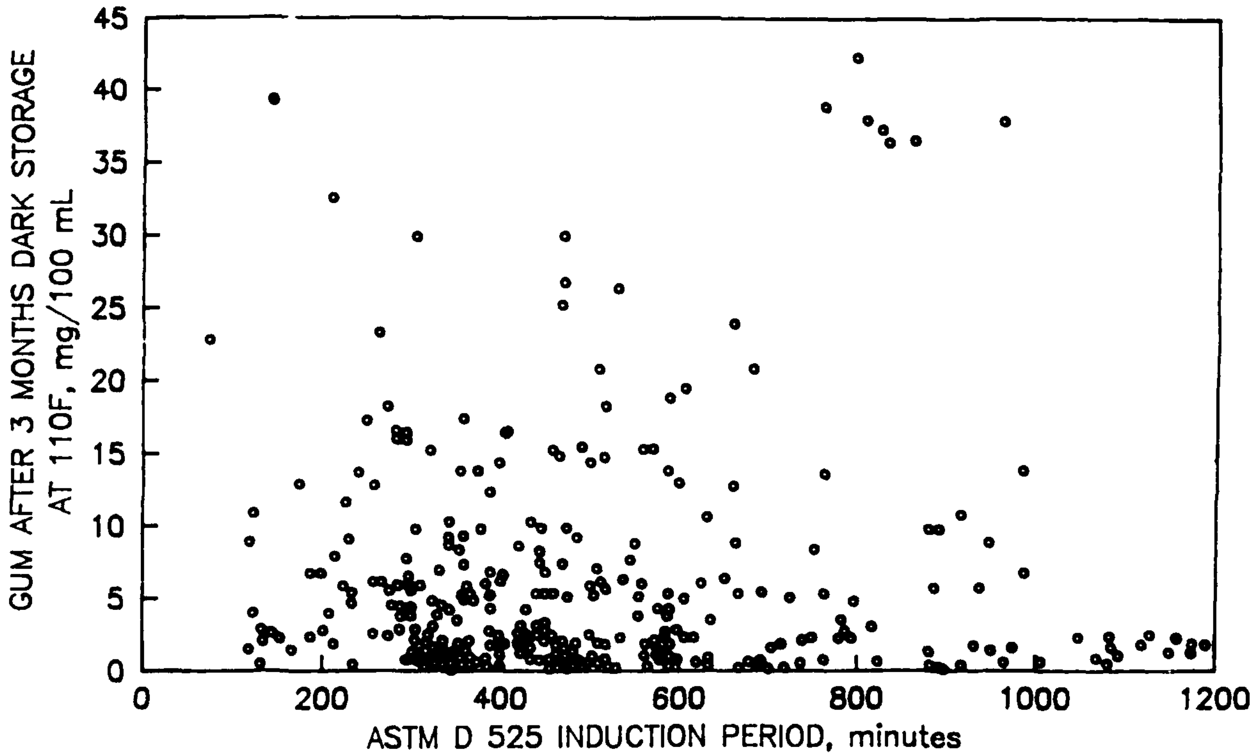

Figure 1. UOP induction period correlation for 3-month dark storage at 110°F (43°C)

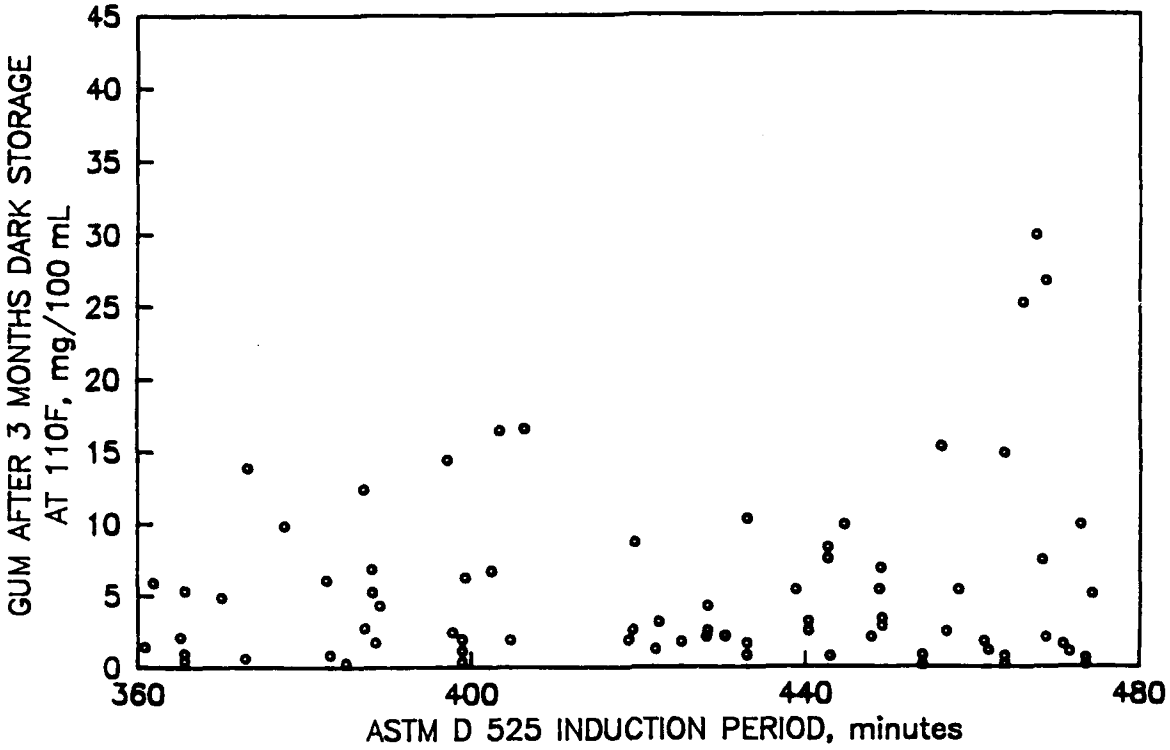

Figure 2. Correlation for 3-month dark storage at 110°F (43°C) at selected induction periods

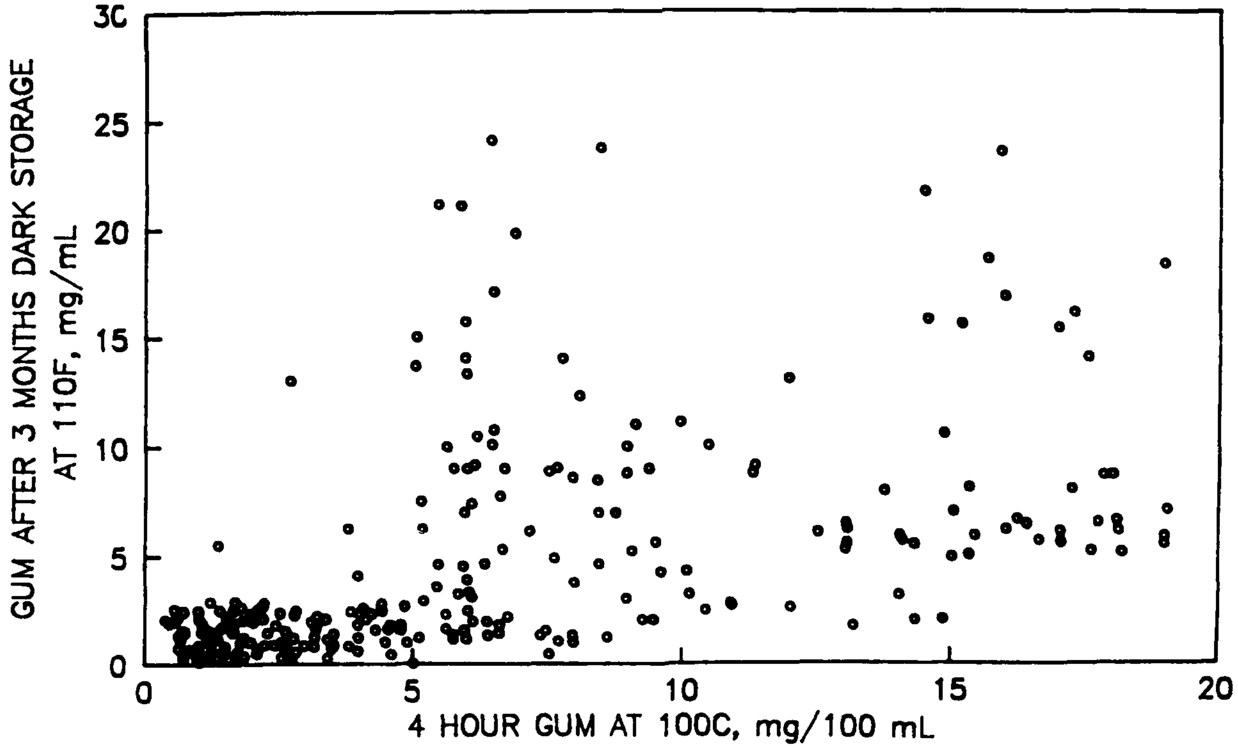

Figure 3. UOP potential gum correlation for 3-month dark storage at 110°F (43°C)

110°F (43°C) storage test. They, therefore, recommend that the "4-hour accelerated gum" be <5 mg/100 mL for successful storage for at least 1 year at ambient (29°C). Storage underground at a lower temperature of 19°C could thus double the storage time to at least 2 years.

Reference 9 provides a summary of gasoline storage data developed in the United States over the years 1952 to 1982. As gasoline deteriorates during aging, gums are formed that are soluble in gasoline and are nonvolatile insoluble deposits when measured by jet evaporation at 162°C in ASTM D 381. These gums and gum precursors form deposits (during evaporation) on hot (air intake) surfaces in engines. Without going into too great a technical depth, gum formation in gasoline has long been recognized as the result of air (oxygen) oxidation of reactive hydrocarbons.(8) Initially, peroxides can be detected at low concentrations long before any other indication of deterioration occurs. Subsequent reactions produce nondescript compounds containing acid, ester, carbonyl, and sulfur groups. Gum formation follows a hydroperoxide polymerization chain reaction mechanism that can be delayed through the addition of antioxidants listed in the gasoline specification (1) and discussed in Reference 8. According to Reference 8, measurement of the peroxide number test provides a measure of the concentration of the initial oxidation product, which is a precursor of gum, and "the presence of peroxides above a peroxide number of 0.5 is a symptom of possible excessive future gum formation." Gasoline process technology and additive technology have greatly impacted commercial gasoline composition. High-severity fluid catalytic cracking (to increase gasoline and middle distillate fuel production) has greatly reduced the storage stability of gasoline blend stocks beginning in the 1960s and even more so in the 1980s as higher boiling, lower quality crudes became available to meet modern petroleum needs. This reduced storage stability is principally related to the formation of troublesome resins that plug filters and small orifices in engine carburetors and gums, which deposit on engine intake system parts and valves.

Historically, deposits form in three major areas of the intake system of engines that accept fuel via carburetion. The engine areas most susceptible to deposit formation have been 1) the carburetor throat, 2) manifold, and 3) the valve port region.(10) In 1966, Johnston and Dimitroff (10) reported the development of a bench test for evaluating induction system depositing (ISD) tendencies of gasolines. They employed fuel aspiration (not injection) and utilized operating conditions of 152° to 204°C, the equilibrium valve-tulip temperatures for a commercially available 2-1/4 horsepower, air-cooled engine. Test results were independent of either the material or surface character of the tube employed to collect deposits, and deposit formation was independent of fuel aromatic or olefin content, length of fuel storage, or sulfur content. The ISD test at 191°C allowed prediction of (small carbureted) engine failure within 2 hours of (160 hour) actual failure times for high ISD-prone fuels used in that era; whereas D 381 gum values failed to predict engine deposits. Johnston and Dimitroff (10) observed that considerably different deposit weights could be obtained if the temperature varied more than 12°C either way from 191°C. Dimitroff and Johnston (11) formulated a mechanism for ISD formation based on chromatographic separation of the fuel precursors into a "dark zone" (plus other components). Infrared (IR) and elemental analysis of the fuel and nuclear magnetic resonance (NMR) analysis of deposits led them to postulate a mechanism involving decomposition and free radical formation, followed by oxidation and molecular recombination of two or three free radicals. Their work showed that deposit precursors are long-chain hydrocarbons containing nitrogen and oxygen, such as amides and carboxylic acids, which are present in gasolines in the parts per million range. However, they used the original (1966 vintage) ISD test and conditions (plus that "era" of fuels).

Johnston and Stavinoha (12) have described an improved ISD procedure for determining the tendencies of a gasoline to form engine intake valve and port deposits. The procedure eventually resulted in Method 500.1 of Federal Test Method Standard No. 791C. Combustion blowby-related recycle gas, a factor known to contribute to unstable gasoline-related valve-tulip deposits, was included in a procedure for analyzing gasoline detergency, described by Marbach, et al. in 1979.(13) This bench procedure simultaneously evaluated fuel deposition tendencies in carburetor throat areas and intake valves. Results were correlated to vehicle fleet test and engine dynamometer test results; however, this work also employed fuel aspiration rather than injection.

During the early to mid-1980s, a large number of automobiles equipped with gasoline engine Multiport Fuel Injection (MPFI) systems encountered injector restriction or "plugging" caused by a buildup of deposits thought to be due to unstable gasoline. These deposits occurred predominantly on the pintle, or small metal tip protruding from the injector and were most detrimental around the orifice area. Effects of injector plugging include a reduction in fuel flow and an erratic spray pattern, resulting in increased engine emissions, poor driveability, hard starting, reduced fuel economy, and loss of power.(14-19)

Temperatures in the injector tip region tend to average close to ambient or somewhat higher during operation, but increase to about 82° to 127°C (depending on engine design) immediately following shutdown of an engine.(15-19) It was believed that during soakback, injectors with high weep rates (those that leak fuel under pressure) tend not to foul, while those injectors with low weep rates foul more severely, and those that close tightly tend not to foul at all. It is believed that soak periods provide an opportunity for unstable gasoline to oxidize and polymerize (20), since only intermittent (and not continuous) engine operation results in MPFI fouling.

Newer MPFI technology results in fuel injection (as contrasted with carburetion or fuel aspiration) directly into the engine manifold port section. Thus, in the modern MPFI engine intake system, there are two principal areas (injector tip and valve tulip) on which fuel-derived troublesome deposits form. These areas experience two different temperature ranges, 82° to 127°C (during soakback) and 127° to 249°C (during engine operation) (21), for the injector tip and valve tulip, respectively. Standard laboratory tests for the determination of gum (ASTM D 381) set forth a temperature of 162°C, which may or may not correspond to the temperature and time frame at which engine deposits actually form. Expensive engine tests have been designed to replace or at least augment the empirical laboratory analytical tests, which have thus far failed to predict engine deposits accurately. A number of nonstandard engine tests are currently being used to investigate MPFI fouling (14) and valve deposition.(22) A bench test incorporating four port injectors is also being utilized as a laboratory test.(23)

Bert, et al. (24) showed in the early 1980s that an additive (polyether amine chemistry) could be applied to remove fuel injector deposits. Flow reductions caused by deposits ranged from 5 to 50 percent of clean injector flow. They found an additive effective for deposit reduction and/or removal in the injectors, carburetor throat, port fuel injector area, and valve port region. The additive also removed combustion chamber deposits. Using fleet and laboratory engine tests, they concluded that the effect is somewhat engine dependent. Other researchers (17) have shown that some additives that keep carburetor sleeves clean may actually contribute to port and valve deposits.

Tupa and Koehler (20) hypothesized a mechanical blockage mechanism whereby evaporated residue from full boiling-range unstable gasolines will gradually oxidize and polymerize to form gums and resins. These materials comprise an adhesive that also holds other particulate matter in place. They also show that gasoline, in the absence of engine effects, can form gum-type deposits in the pintle area upon soaking for 18 days at 90°C. Benson and Yaccarino (16) calculated that a deposit layer only 6 micrometers thick on both pintle and orifice would restrict fuel flow through an injector by 26 percent.

Lenane and Stocky (25) analyzed MPFI deposits by FTIR spectroscopy and concluded that the deposits were primarily carbon, with sulfur being the prevalent inorganic element. The spectra showed the presence of oxidized hydrocarbons and unsaturates (the oxidized materials were carboxylic acids, not ketones and esters typical of oxidized motor oil components). Sulfates, indicative of sulfonate detergents in lubricants, were also found. Taniguchi, et al. (17) used electron spectroscopy for chemical analyses (ESCA) to show that deposit composition is uniform throughout its entire thickness on the pintle. Their results showed that three stability-related constituents of gasoline (sulfur, diolefins, and polar compounds) affect the rate of injector deposit formation. Both olefins (commonly found in modern gasolines) and diolefins (not present in petroleum crude oils) readily oxidize during storage to form gums and resins.

In 1986, the Coordinating Research Council, Inc. (CRC) solicited proposals to address the development of an injector deposit bench test rig. Work sponsored by CRC at Southwest Research Institute (15) resulted in a bench test procedure using equipment reported in Reference 13, which ranked fuels of known depositing ability, but failed to properly rank the same fuels treated with modern deposit control (detergent) additives.

The "Clean Air Act of 1990" will lead to "clean air" gasoline (i.e., reformulated gasoline) fuels that must be qualified as meeting various emissions requirements.(23) Both oxygenates and detergent additives ("deposit control additives") are major constituents of future reformulated gasoline for ozone and carbon monoxide control.

For the purposes of the current report on the evaluation of motor gasoline stability, test techniques are employed that are applicable to fuels and fuel blend stocks not containing detergents. Methodology for evaluating stability-related aspects of modern commercial fuels employing detergents and their impact on engine operation are under development in reformulated gasoline-related programs.

III. EXPERIMENTAL APPROACH

This program encompassed darkroom storage of test fuels at ambient (San Antonio, TX) for time periods up to 4 years, at 43°C (110°F) for 48 weeks and at 54°C (130°F) for 24 weeks. These storage times varied considerably in the different phases of the work. TABLE 2 is a summary of accelerated test-time factors for predicting storage time at various temperatures and at various oxygen concentrations including atmospheric air (3.1 psi oxygen) using two different mathematical relations, Methods "A" and "B."

Method A is the rule of rate doubling for each 10°C increase in temperature and tenfold increase in going to 3.1 psi (partial pressure of oxygen in air at atmospheric pressure) from 100 psi oxygen, which was used in the 100°C ASTM D 873 (modified) testing. The other accelerated tests at 43° and 54°C were performed at atmospheric pressure (14.7 psi, 3.1 psi oxygen). The utility of the Method A calculations have recently been reemphasized for diesel fuel stability applications.(26)

The factors for Method B use the Arrhenius equation as developed by Cole and Nixon.(27) While Method B is more conservative than Method A, it was developed using desert storage conditions for jet fuels including military JP-4 and an energy of activation of 20.5 kilocalories per gram-mole. This relationship is particularly useful for fuels that degrade as a function of availability of oxygen, especially true of gasoline.

TABLE 2. Accelerated Test-Time Factors for Predicting °C Storage Time Under Various Oxygen (O_2) Pressures*

Accelerated Test		Storage Temperature	Multiplication Factors for Predicting Time Factors at Various Oxygen (O_2) Pressures			
O_2 Pressure psi	Temperature °C	°C	100 psi O_2	3.1 psi O_2	1.5 psi O_2	0.1 psi O_2
Method A: Rate Doubled for Each 10°C Above Storage Temperature						
100	100	100	1	10	20	--
		90	2	20	40	--
		80	4	40	80	--
		70	8	80	160	--
		60	16	160	320	--
		50	32	320	640	--
		40	64	640	1,280	--
		30	128	1,280	2,560	--
		20	256	2,560	5,120	--
		10	512	5,120	10,240	--
3.1	100	100	--	1	2	--
		90	--	2	4	--
		80	--	4	8	--
		70	--	6	16	--
		60	--	16	32	--
		50	--	32	64	--
		40	--	64	128	--
		30	--	128	256	--
		20	--	256	512	--
		10	--	512	1,024	--
3.1	54	54	--	1	2	--
		44	--	2	4	--
		34	--	4	8	--
		24	--	8	16	--
		14	--	16	32	--
		4	--	32	64	--
3.1	43	43	--	1	2	--
		33	--	2	4	--
		23	--	4	8	--
		13	--	8	16	--
		3	--	16	32	--
Method B: Arrhenius Equation: $\log (t_2/t_1) = 4500 (1/T_2 - 1/T_1) - 0.52 \log (P_2/P_1)$						
100	100	100	1	6	9	36
		90	2	13	19	78
		80	5	29	43	175
		70	11	69	101	412
		60	28	171	250	1,022
		50	74	449	655	2,676
		40	205	1,250	1,823	7,456
		30	613	3,731	5,442	22,250
		20	1,968	11,980	17,476	71,450
		10	6,866	41,802	60,973	246,000
3.1	100	100	--	1	2	6
		90	--	2	3	13
		80	--	5	7	29
		70	--	11	17	68
		60	--	28	41	168
		50	--	74	108	440
		40	--	205	298	1,225
		30	--	613	900	3,654
		20	--	1,968	2,910	11,736
		10	--	6,866	10,091	40,946
3.1	54	54	--	1	2	6
		44	--	3	4	16
		34	--	8	12	47
		24	--	25	36	146
		14	--	83	121	495
		4	--	305	445	1,818
3.1	43	43	--	1	2	6
		33	--	3	4	17
		23	--	9	13	55
		13	--	31	46	186
		3	--	116	169	691

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* Assumes gas ullage volume to liquid fuel volume size ratio is sufficient so as not to reduce oxygen pressure due to reaction, i.e., assumes no oxygen reduction through starvation.

Oxygen available in the ullage above fuel in underground storage tanks is expected to be low due to oxygen starvation by reduction of ullage breathing under isothermal storage conditions. For the factors in TABLE 2, it is assumed that a large gas ullage to liquid volume exists, usually a minimum ratio of 1:3 (1 part air to 3 parts fuel) in laboratory tests, such that the oxygen availability is not diminished to the point of oxygen starvation below the oxygen values as stated. Oxygen starvation to lower oxygen values results in larger mathematical factors for predicting possible storage time or storage life.

To use the factors in TABLE 2, find the accelerated test conditions of oxygen partial pressure and temperature on the left side of TABLE 2 and then locate the desired storage temperature and assumed oxygen partial pressure to find the multiplication factor for storage life.

As an example, using "Method A" 1 hour at 100°C and 100 psi oxygen has a factor of 2,560 for storage at 20°C and 3.1 psi oxygen. Thus, 6 hours at 100°C (and 100 psi) would give 15,360 hours at 20°C (and 3.1 psi) or 640 days or 91.4 weeks or 1.76 years. Thus, the "6-hour D 873 modified test" time to reach a similar gum level would be 1.76 years at a storage temperature of 20°C or 3.5 years at a storage temperature of 10°C, which perhaps might be expected to be the average storage temperature in NATO CEPS storage. "Method B" would give values of 8.2 years and 28.7 years at 20° and 10°C, respectively.

Lower oxygen pressures present in long-term storage of sealed tanks would give higher storage factors as indicated in TABLE 2.

Figs. 4 and 5 provide the ambient room temperature and the fuel temperature (of a control sample) in 5-gallon metal storage cans (filled one third full with test fuels) during a 1-year time span. Aeration of the test samples was at each sampling period.

Samples were subjected to a battery of physical and chemical tests prior to storage and again at selected storage times. These tests included determination of (1) Induction Period (ASTM D 525), (2) Unwashed and Existent Gum (ASTM D 381), (3) Peroxide Number (UOP Method 33-82),

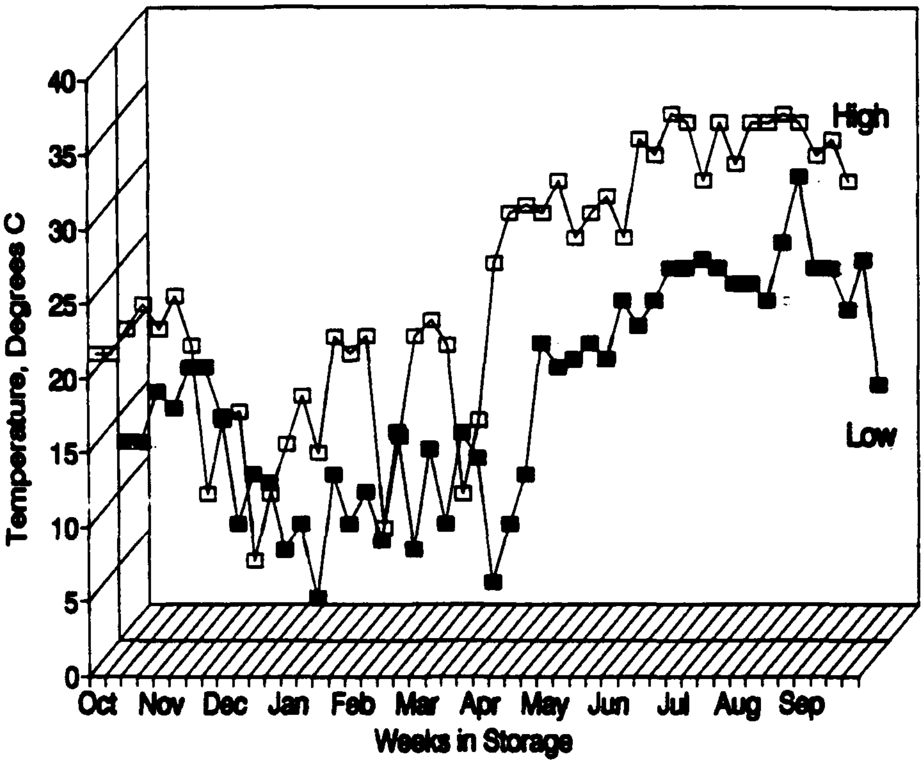

Figure 4. Storage room ambient temperature range (October 1986 to September 1987)

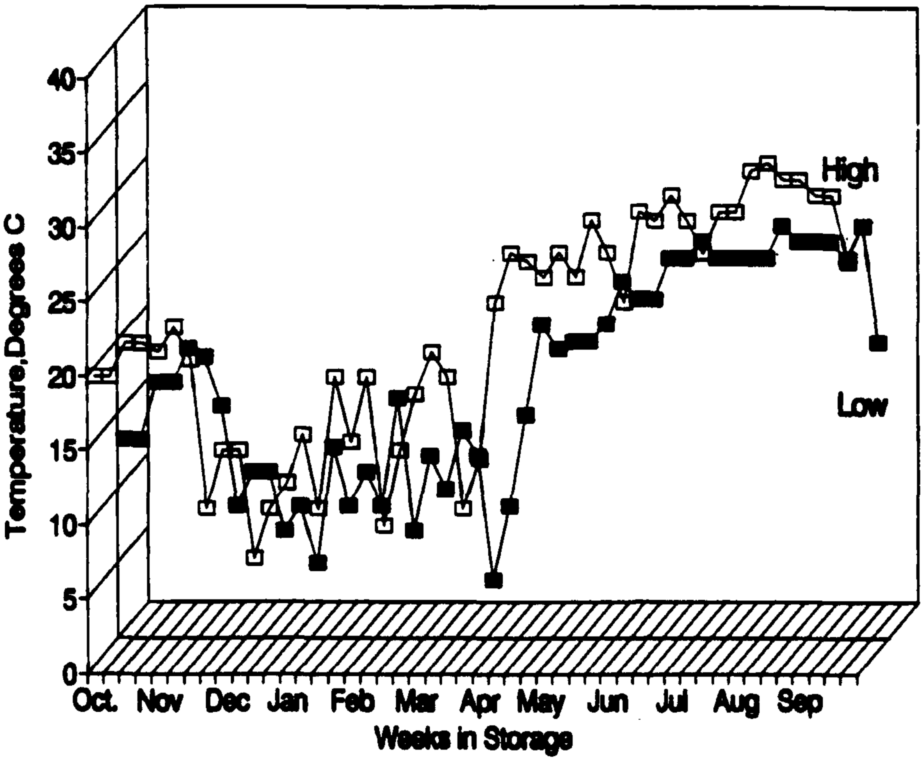

Figure 5. Temperature of fuel samples (ambient storage, October 1986 to September 1987)

(4) Color (ASTM D 1500 and D 156), and (5) Induction System Deposit (ISD) Rating (Method 500.1, Federal Test Method Standard 791C). Wall-adhered insoluble gum and filterable precipitate were obtained, where appropriate, by a modification to U.S. Bureau of Mines methodology.(7) Additionally, ASTM D 873 oxidation stability methodology was applied to all blends prior to storage. These tests relate to properties of gasoline that have been traditionally evaluated for gasoline storage stability and that relate to gasoline engine fuel utilization system requirements.

In the D 873 "X-hour" aging procedure, the 100-mL sample (after "X-hour" aging) is transferred to a flask, and the sample container is washed twice with 10-mL portions of gum solvent (toluene-acetone mixture). The solvent washings are also placed in the flask. The flask material is divided equally into two gum beakers and the unwashed gum determined by ASTM Method D 381 (air jet). The sum of the increase in weight of the two gum beakers is reported as "X-hour" total unwashed gum in mg/100 mL and (after heptane washing) as total existent gum in mg/100 mL. This test procedure prepared in ASTM format is provided as Appendix B. Appendix C covers "Flashing of Sample During Gum Determination by ASTM D 381, NATO Gasoline Stability Program," Appendix D covers "Change in Composition Recommended for Reference Gasoline; MIL-G-53042" and Appendix E presents "Data Summary Figures" covering the data generated in this project.

The program has evolved into four distinct test phases, numbered sequentially. Each test phase was performed with samples uniquely selected to permit several approaches to be made. Also, obtaining "refinery fresh" gasoline samples having low (360 minute) induction periods and still meeting specification restrictions of no detergents was almost impossible.

Phase I: An unstable (via caustic treating) light catalytically cracked naphtha blend stock was incorporated into a stable, leaded regular gasoline to provide five fuel blends, plus the original two materials, for initial study.

Phase II: An unleaded gasoline plus nine refinery components (which make up gasoline) were obtained. Five "hand blends" of the components were also prepared, and two miscellaneous materials of interest (the reference gasoline of MIL-G-53042 (28), and a pyrolysis naphtha from a chemical plant) were included to provide 18 total samples for this test phase.

Phase III: Eight "artificial" fuel blends were prepared whose commonality is a "low" induction period, but which represent both "good" and "bad" fuels based on D 381 gum data and D 873 modified potential gum.

Phase IV: This final test phase incorporated four "low" induction period fuels that were commercially available, a debutanizer bottom sample, and a blend of debutanizer bottom with regular leaded gasoline.

Engine Tests: Special engine tests for evaluation of carburetor and valve-tulip depositing tendencies were conducted on three gasolines, two of which contained different percentages of light catalytically cracked gasoline.

IV. DISCUSSION

TABLE 3 is a summary of code numbers and descriptive information for the samples in test Phases I through IV.

TABLES 4 and 5 summarize selected aging test data for Phase II and Phases I, III, and IV, respectively. All data generated are provided in Appendix E as graphs of unwashed gum, existent gum, peroxide number, and ISD rating for each of the phases. A general correlation trend can be noted between the existent gum, peroxide number, and ISD rating in ambient, 43°C, and 54°C storage. The relationship of these test results at the same three test temperatures varies considerably, so much so that the ranking of fuels by stability at one temperature may not be the same at one or both of the other temperatures. The data in Appendix E are discussed here by the four phases.

TABLE 3. Summary of Sample Characterization Data

AL-Code No.	Sample Description	Induction Period, D 525, minutes	Gravity, °API	Distillation, °F								Hydrocarbon Type, FIA, vol%			Octane No.		
				IBP	10% E	20% E	50% E	90% E	EP	Res	Loss	Sats	Olef	Arom	RON	MON	RVP
Phase I																	
14158-G	100% LCC Gasoline	240	54.8	115	150	168	235	380	427	1.0	1.0	39.5	34.9	25.6	--	--	–
14388-G	75% LCC, 25% Regular Leaded Gasoline	250	55.0	111	153	175	239	376	447	1.0	1.0	--	--	--	--	--	–
14389-G	50% LCC, 50% Regular Leaded Gasoline	345	56.3	103	147	173	234	351	422	1.0	1.0	--	--	--	--	--	–
14390-G	40% LCC, 60% Regular Leaded Gasoline	465	56.6	101	145	174	234	347	420	1.0	1.0	--	--	--	--	--	–
14391-G	35% LCC, 65% Regular Leaded Gasoline	900	57.0	100	147	175	233	342	416	1.0	1.0	--	--	--	--	--	–
14392-G	30% LCC, 70% Regular Leaded Gasoline	>960	56.4	101	152	180	234	333	414	1.0	1.0	--	--	--	--	--	–
13893-G	100% Regular Leaded Gasoline	>960	58.9	99	134	165	226	295	366	0.5	0.0	71.1	0.9	28.0	--	--	–
Phase II																	
15271-G	HC Naphtha	>2490	82.4	95	108	111	123	152	170	0.0	1.0	98.1	0.0	1.9	84	81	12.5
15272-G	Reformate	>6015	42.2	103	178	212	261	329	418	1.0	1.0	34.1	1.5	64.4	100	88	6.1
15273-G	HSR Naphtha	>5835	59.6	190	227	226	260	314	349	1.0	0.0	88.0	0.7	11.3	54	53	1.1
15274-G	LSR Naphtha	>4620	79.6	89	109	113	129	177	224	0.0	1.0	97.3	0.0	2.7	75	73	12.6
15275-G	Alkylate	>2640	64.3	99	133	151	207	327	477	1.0	1.0	90.8	1.1	8.1	72	70	7.5
15276-G	No-Lead Gasoline	870	58.3	89	123	142	205	327	397	1.0	1.0	49.5	20.6	29.9	93	81	8.8
15277-G	HCC Naphtha	900	48.3	108	176	205	266	348	401	1.0	0.0	38.0	18.5	43.5	94	81	4.7
15278-G	LCC Naphtha	435	60.4	93	122	139	185	297	368	1.0	1.0	34.8	32.7	27.5	95	81	9.5
15279-G	Coker Naphtha	105	80.8	89	104	109	122	162	202	1.0	1.0	52.1	46.3	1.6	85	74	13.7
15280-G	Raffinate	4440	76.8	139	155	150	167	188	200	1.0	0.0	95.4	2.7	1.9	63	62	5.5
15281-G	Pyrolysis Gasoline	105	51.7	97	111	116	136	315	370	1.0	1.0	17.0	40.7	42.3	97	80	10.6
15282-G	Referee Blend, MIL-G-53042	795	68.6	203	214	216	223	244	253	1.0	0.0	79.6	19.2	1.2	38	37	1.6
15283-G	1/3 HC, 1/3 Ref, 1/3 HSR	4560	57.6	105	144	162	226	321	390	1.0	1.0	73.4	0.7	25.9	79	74	6.5
15284-G	1/3 Ref, 1/3 HSR, 1/3 LSR	6000	57.4	100	142	162	226	312	381	0.5	0.0	73.1	0.7	26.2	76	71	6.6
15285-G	1/3 HSR, 1/3 LSR, 1/3 Aklylate	4574	65.2	102	133	149	207	312	420	1.0	0.0	92.0	0.6	7.4	67	65	7.0
15286-G	1/3 HSR, 1/3 Alkylate, 1/3 LCC	1275	59.7	104	147	171	231	318	425	0.5	0.0	72.9	11.5	15.6	74	68	6.0
15287-G	1/2 HCC, 1/2 LCC	750	53.9	97	140	164	232	334	414	0.5	0.0	38.9	25.6	35.5	95	81	7.1
15288-G	Coker Naphtha Plus Antioxidant	1770	80.3	90	106	110	123	168	228	0.5	0.0	52.1	46.3	1.6	86	74	13.7
Phase III																	
15707-G	Refinery C MPFI Batch No. 4	240	59.0	76	111	138	220	364	427	1.0	1.0	54.3	15.0	30.7	91	81	11.2
15815-G	MIL-G-53042 Reference Gas + 0.25% Diolefin	435	66.7	210	216	218	226	250	265	1.0	1.0	79.1	19.2	1.7	45	43	1.5
15949-G	Refinery A Coker Naphtha	240	52.4	194	229	245	291	364	401	0.5	1.0	46.3	38.7	15.0	64	60	1.3
15963-G	55% Coker Naphtha, 45% No-Lead Gasoline (15276-G)	315	54.7	110	162	192	264	355	408	1.0	2.0	48.8	29.0	22.2	78	70	4.7
15964-G	55% Coker Naphtha, 45% Light Cat. Cracked	315	55.5	110	157	185	257	354	400	1.0	2.0	45.1	33.9	21.0	79	70	5.2
16004-G	Refinery B Coker Naphtha	75	81.5	95	107	–	119	155	193	--	–	55.2	43.2	1.6	85	75	13.2
16021-G	65% Refinery C MPFI Batch No. 4 + 25% No-Lead Gasoline (15276-G)	360	58.0	87	117	140	218	367	459	1.0	2.0	52.2	16.3	31.5	92	81	9.7
16023-G	67% Refinery B Coker (16004-G) + 33% No-Lead Gasoline (15276-G)	375	72.7	95	111	126	135	270	380	1.0	3.0	51.4	37.9	10.7	88	77	1.4
Phase IV																	
16798-G	Debutanizer Bottoms	195	58.7	102	134	149	208	337	402	0.5	0.5	40.4	33.5	26.1	--	--	6.9
16813-G	Commercial Co. A Unleaded Gasoline	705	58.6	--	--	--	--	--	--	--	--	59.8	9.6	30.6	--	--	--
16815-G	Commercial Co. B Regular UnLeaded Gasoline	315	61.4	--	--	--	--	--	--	--	--	58.6	14.9	26.5	--	--	--
16816-G	Commercial Co. B Regular Leaded Gasoline	315	62.9	--	--	--	--	--	--	--	--	60.5	13.5	26.0	--	--	--
16817-G	Commercial Co. C Regular Unleaded Gasoline	780	57.6	--	--	--	--	--	--	--	--	45.7	24.7	29.6	--	--	--
16832-G	45% Debutanizer Bottoms, 55% Unleaded Gasoline (13892-G)	345	58.7	--	--	--	--	--	--	--	--	60.3	11.3	28.4	--	--	--

TABLE 4. Selected Aging Test Data for Phase II

AL-Code No.	Sample Description	Induction Period, D 525, minutes	4-Hour Modified D 873		6-Hour Modified D 873		8-Hour Modified D 873		D 381, Gum, mg/100 mL								D 381, Gum, mg/100 mL
			Gum, mg/100 mL		Gum, mg/100 mL		Gum, mg/100 mL		Existent								Unwashed
			Unwashed	Existent	Unwashed	Existent	Unwashed	Existent	I	43°C	54°C	Ambient Storage					Initial
									0	24 wk	12 wk	64 wk	96 wk	144 wk	176 wk	208 wk	
Phase II																	
15271-G	HC Naphtha	>2490	0.5	--	0.1	--	0.9	--	0.5	0.0	0.4	0.2	0.2	0.1	0.8	0.0	0.8
15272-G	Reformate	>6015	4.0	--	2.9	--	3.0	--	0.1	1.9	3.9	0.2	1.2	1.6	2.0	2.0	1.5
15273-G	HSR Naphtha	>5835	3.2	--	3.7	--	2.9	--	0.4	0.0	0.3	0.5	0.4	0.3	0.9	0.0	2.6
15274-G	LSR Naphtha	>4620	1.2	--	0.5	--	1.2	--	0.0	0.0	0.3	0.2	0.4	0.1	0.6	1.0	0.2
15275-G	Alkylate	>2640	1.9	--	1.3	--	2.0	--	0.0	0.0	0.2	0.7	0.0	1.3	0.9	0.6	0.4
15276-G	No-Lead Gasoline	870	2.4	--	3.5	--	5.7	--	0.4	0.4	1.6	0.9	1.0	1.0	1.6	2.1	1.2
15277-G	HCC Naphtha	900	4.3	--	6.9	--	13	--	0.4	5.2	4.2	2.8	3.7	4.4	4.1	4.4	0.9
15278-G	LCC Naphtha	435	2.6	--	4.2	--	15	--	0.0	1.7	1.4	0.6	1.1	1.6	1.4	1.4	0.6
15279-G	Coker Naphtha	105	49	--	(>49)	--	(>49)	--	0.6	2.2	1.6	1.1	1.2	1.8	2.4	3.6	13.8
15288-G	Coker + AO	>1770	7.2	--	15	--	12	--	0.8	1.8	0.7	0.3	0.9	0.7	0.4	1.1	16.4
15280-G	Raffinate	>4440	2.0	--	0.4	--	1.5	--	0.5	0.8	0.2	0.1	0.3	0.0	0.5	0.7	1.3
15281-G	Pyrolysis Gasoline	105	775	--	(>775)	--	(>775)	--	5.1	14	88	15	16	25	51	88	22.8
15282-G	Referee Blend	795	0.0	--	0.1	--	0.0	--	0.6	1.7	0.9	0.0	0.7	0.0	0.5	0.0	1.5
15283-G	1/3 HC, 1/3 Ref, 1/3 HSR	>4560	1.9	--	2.2	--	2.9	--	0.6	0.9	0.4	1.0	0.5	0.1	1.6	1.3	3.1
15284-G	1/3 Ref, 1/3 HSR, 1/3 L	>6000	1.1	--	2.1	--	1.6	--	0.7	1.2	0.2	0.8	0.4	0.0	1.5	NES*	1.5
15285-G	1/3 HSR, 1/3 LSR, 1/3 Alky	>4574	2.0	--	1.1	--	1.5	--	0.6	0.5	0.0	0.9	0.4	0.3	0.6	0.5	0.7
15286-G	1/3 HSR, 1/3 Alky, 1/3 LCC	1275	1.9	--	1.9	--	2.0	--	0.4	1.5	0.5	0.4	0.7	0.7	1.0	0.7	0.8
15287-G	1/2 HCC, 1/2 LCC	750	4.0	--	5.3	--	11	--	0.6	4.0	2.9	1.7	2.7	2.8	3.2	3.0	1.3

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* NES = Due to an earlier container leak, there is not enough sample for further evaluation.

TABLE 5. Selected Aging Test Data for Phases I, III, and IV

AL-Code No.	Sample Description	Induction Period, D 525, minutes	4-Hour Modified D 873 Gum, mg/100 mL		6-Hour (or Other) Modified D 873 Gum, mg/100 mL		D 381, Gum, mg/100 mL Existent										D 381, Gum, mg/100 mL Unwashed
			Unwashed	Existent	Unwashed	Existent	I	43°C		54°C	Ambient Storage						Initial
							0	24 wk	40 wk	16 wk	64 wk	96 wk	128 wk	144 wk	176 wk	208 wk	
Phase I																	
14158-G	100% LCC Gasoline	240	59	--	(>59)	–	1.9	4.5	37	56	4.9	2.3	4.4	4.7	6.9	7.7	11.8
14388-G	75% LCC, 25% Regular Leaded Gasoline	250	25	–	54 (4.5 hr)	–	1.4	3.9	15	53	3.7	1.6	4.5	4.2	5.8	7.4	8.5
										20 wk							
14389-G	50% LCC, 50% Regular Leaded Gasoline	345	8.3	–	48 (4.8 hr)	–	0.2	4.1	103	38	2.5	2.0	3.7	4.9	22	76	5.5
14390-G	40% LCC, 60% Regular Leaded Gasoline	465	4.7	–	33	–	1.1	2.2	67	38	3.0	3.4	16	24	40	42	5.3
14391-G	35% LCC, 65% Regular Leaded Gasoline	>900	5.2	–	16	–	0.0	41	264	32	1.3	1.5	4.8	6.8	15	22	3.9
14392-G	30% LCC, 70% Regular Leaded Gasoline	>960	5.3	–	17	–	0.6	54	262	36	0.8	0.8	1.6	3.2	4.5	8.5	4.7
13893-G	100% Regular Leaded Gasoline	>960	2.0	–	1.5	–	0.5	0.2	0.3	0.9	0.7	0.2	0.1	0.2	1.2	2.4	0.6
										12 wk							
Phase III																	
15707-G	Refinery C MPPI High Deposit Fuel Batch No. 4	240	174	169	–	(>170)	4.3	15	–	14	5.8	19	76	104	204	449	7.3
15815-G	MIL-G-53042 Reference Gasoline + 0.25% Diolefin	435	15	15	65	64	0.2	0.4	–	2.1	0.0	0.0	0.0	0.6	0.4	0.2	0.8
15949-G	Refinery A Coker Naphtha	240	280	275	–	(>275)	34	34	–	29	32	38	48	39	37	49	34.5
15963-G	55% Refinery A Coker Naphtha (15949) 45% Unleaded Gasoline (15276)	315	155	154	–	(>154)	15	18	–	18	18	17	26	22	21	23	15.6
15964-G	55% Refinery A Coker Naphtha (15949) 45% LCC Naphtha (15278)	315	148	144	–	(>144)	18	19	–	16	17	21	24	17	19	20	18.8
										22 wk							
16004-G	Refinery B Coker Naphtha	75	318	310	–	(>310)	0.6	1.4	–	0.8	5.1	27	31	18	17	NES	2.0
16021-G	75% Refinery C (15707) + Unleaded Gasoline (15276)	360	30	18	125	112	4.5	8.2	–	9.3	5.0	6.0	6.8	7.5	16	9.7	8.8
16023-G	67% Refinery B Coker Naphtha (16004) + Unleaded Gasoline (15276)	375	4.5	3.7	35	32	0.4	1.4	–	1.5	0.8	0.4	1.3	1.1	1.1	1.3	0.6
									48 wk	24 wk							
Phase IV																	
16798-G	Debutanizer Bottoms	195	231	225	–	(>225)	1.6	5.0	6.5	6.3	3.4	4.0	4.5	5.0	7.0	–	2.9
16813-G	Commercial Co. A Unleaded	705	16	0.4	15	0.3	0.0	0.2	1.0	1.9	0.6	0.2	0.4	0.6	0.3	–	13.8
16815-G	Commercial Co. B Regular Unleaded	315	29	16	94	88	0.0	2.5	5.2	3.4	0.5	1.2	3.6	6.3	12	–	21.0
16816-G	Commercial Co. B Regular Leaded	390	52	36	154	116	0.1	2.5	3.4	4.7	0.8	8.7	18	NES*	NES	–	14.4
16817-G	Commercial Co. C Regular Unleaded	780	5.3	2.5	7.5	4.5	0.0	2.6	2.7	2.7	2.2	1.1	5.2	4.1	5.3	–	5.2
16832-G	45% Debutanizer Bottoms/55% of 13892-G (Reg. Leaded Gasoline)	345	12	10	67	65	3.1, 0.9	3.8	4.8	5.5	1.3	2.1	1.7	1.8	1.7	–	3.8

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* NES = Due to an earlier container leak, there is not enough sample for further evaluation.

A. Phase I

For Phase I, Fig. 6 summarizes the relation of D 873 data to gum levels at 208 weeks of ambient storage for regular gasoline and various amounts of catalytic-cracked gasoline added to it to reduce the D 525 induction period. Selection of a limit of 5 mg/100 mL for D 873, 6-hour test, is shown to expect the ambient storage samples to remain below a D 381 gum value of 5 mg/100 mL in ambient storage. To estimate the equivalence of 1-year storage at ambient temperature to accelerated storage at both 43° and 54°C, Arrhenius relationships were employed. Energies of Activation, Ea, were calculated for the seven gasolines in the first part of this program. The majority of the values were found to be in the range of 15 to 20 kcal/g mole. The Arrhenius relationship between storage time (to form a given level of deposits) and storage temperature (in degrees Kelvin) is (29):

$$\text{Log } t_2/t_1 = (Ea/2.3R)\,(1/T_2 - 1/T_1) - B \text{ Log } (P_2/P_1)$$

where: Ea = Energy of Activation

R = Gas constant (1.9782 cal/°K-mole)

t_2 = Time in storage at T_2 (in degrees Kelvin)

t_1 = Time in storage at T_1 (in degrees Kelvin)

B = Pressure constant

P_2 = Partial pressure of oxygen in ullage of storage vessel 2

P_1 = Partial pressure of oxygen in ullage of storage vessel 1

Based on an Ea of 20.5 kcal/g mole estimated for fuels in this program (and used in TABLE 2), the time relationship is as follows:

> The equivalent of 1 year at 25°C (San Antonio estimated average ambient temperature) is 7.1 weeks at 43°C and 2.5 weeks at 54°C. The equivalent of 1-year storage at 19.4°C, which probably is closer to the average ambient temperature in Europe, is 3.8 weeks at 43°C and 1.3 weeks at 54°C.

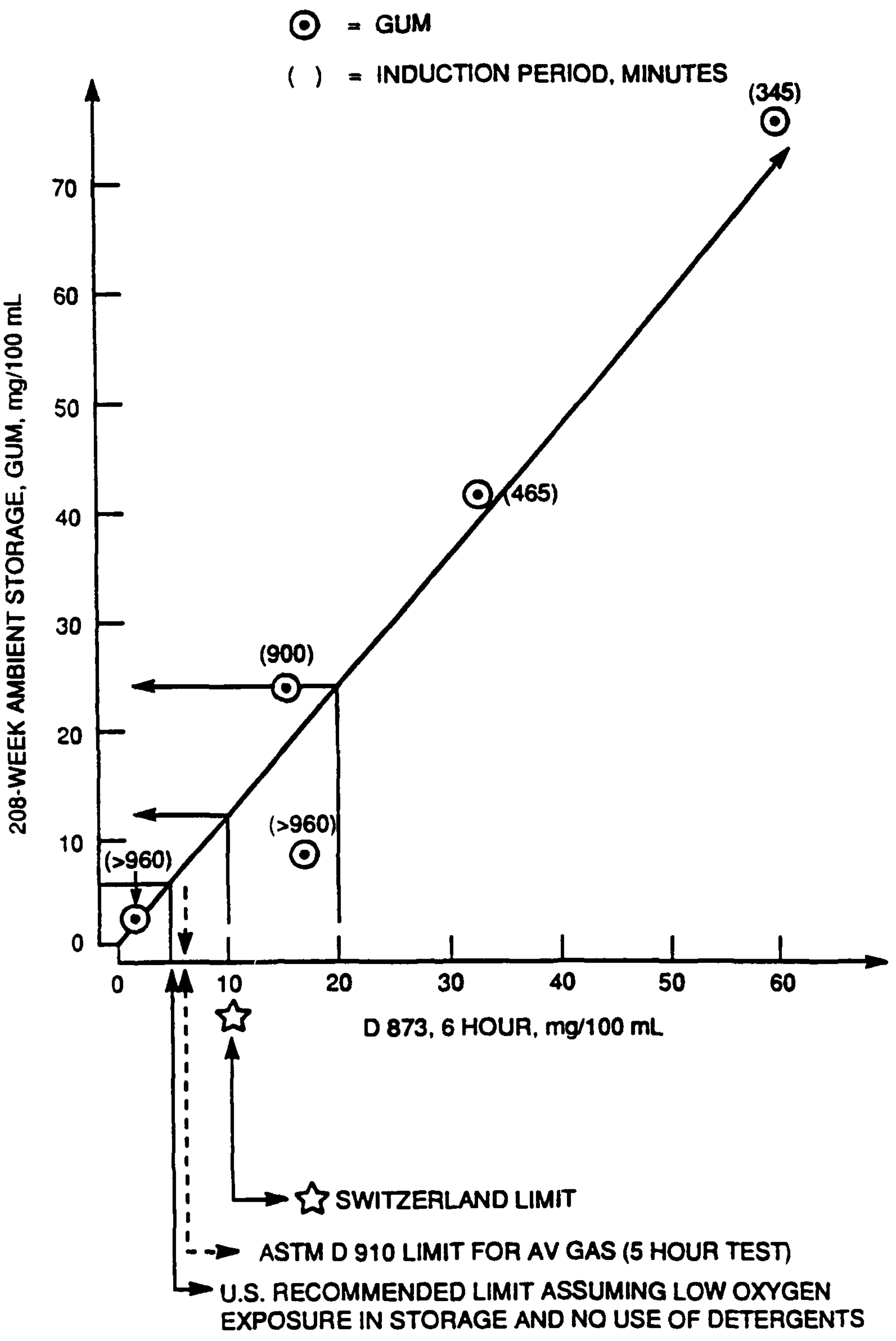


Figure 6. Phase I: regular gasoline plus catalytic cracked gasoline blend stock

It has been stated that if the 4-hour D 873 type test results are <5 mg/100 mL, then the 3-month 43°C storage results will be <3 mg/100 mL, which means the fuel will be stable for 1 year at ambient temperatures.(8) One year at ambient temperature of 23°C would be equivalent to 2 years at 13°C.

Thus, in evaluating the data in TABLES 4 and 5 and graphically in Appendix E, it has been assumed that 6 hours at 100°C (D 873 modified test) relates to 2 years at 23°C or 4 years at 13°C. It has been stated that stored product temperature is fairly stable throughout the year at approximately 10° ± 6°C in Central European Pipeline System (CEPS) storage tanks that are semiburied (cut and cover).(30)

At each of the sampling periods for the ambient storage, the 5-gallon can was brought to laboratory room temperature overnight, sampled, and returned to ambient temperature; thus, aeration was minimal and occurred only at the test intervals. Setting the recommended D 873, 6-hour gum limit of 5 mg/100 mL was thus based on low oxygen exposure in actual storage and no use of fuel detergents as it is not known if the tests employed will correlate with engine deposits when modern detergents are used to formulate gasolines. (Refer to background for discussion of modern detergents and formulated gasolines.) The MIL-G-3056 specification does not allow the use of detergents (now common in commercial gasolines).

Use of vented 43°C storage in Phase I was abandoned (due to high evaporation levels) in favor of aeration of sealed sample vessels at sampling periods in subsequent phases as was also the procedure for 54°C storage and ambient storage.

B. Phase II

For Phase II samples, Fig. 7 summarizes D 873, 8-hour gum data and 54°C, 12-week gum data (which were essentially the same as 43°C gum data at 24 weeks). The 8-hour data were chosen compared to the 6-hour data because of the predominantly low values. Note that only coker naphtha and pyrolysis gasoline greatly exceed 15 mg/100 mL, the approximate value for the next

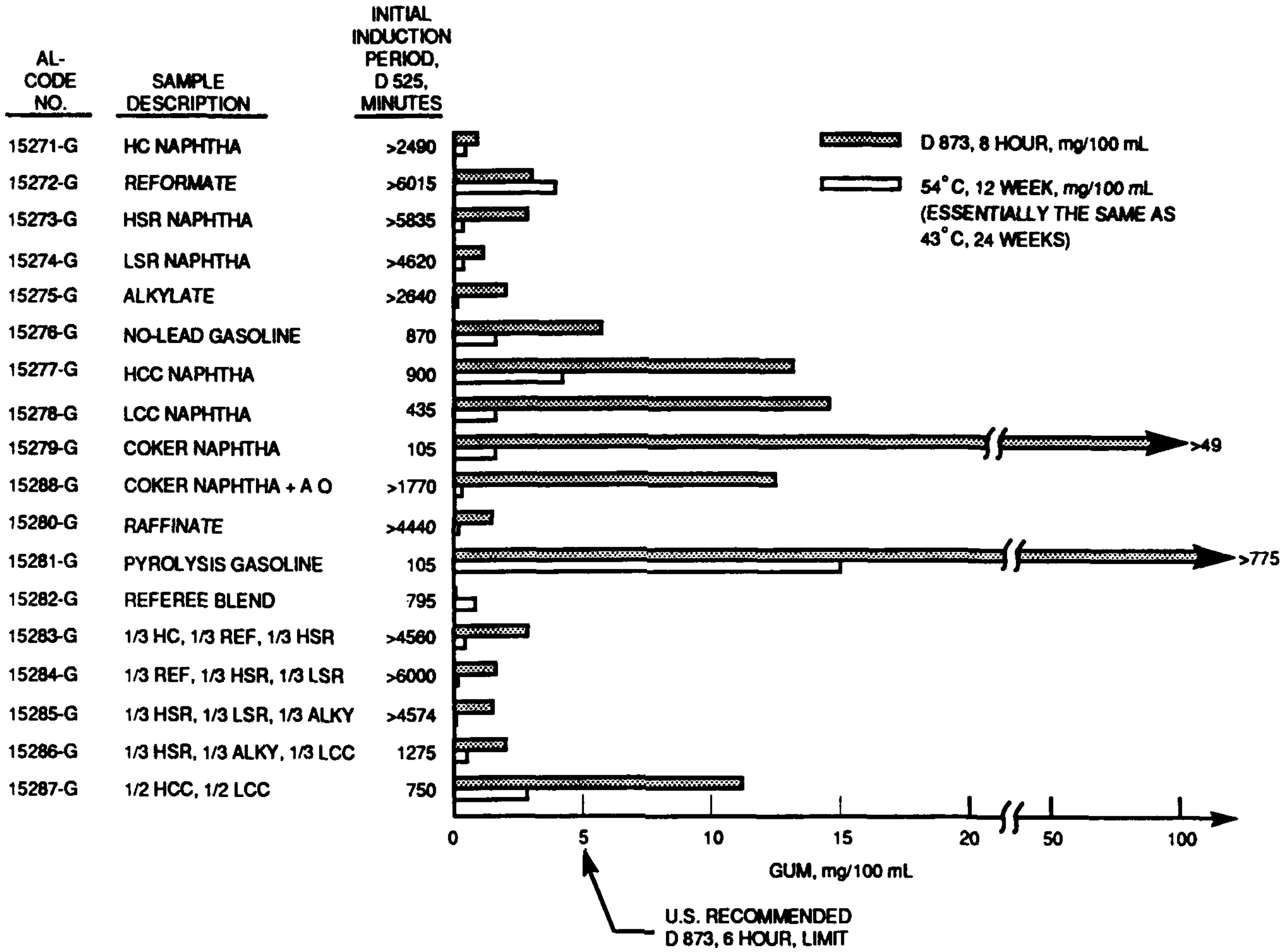


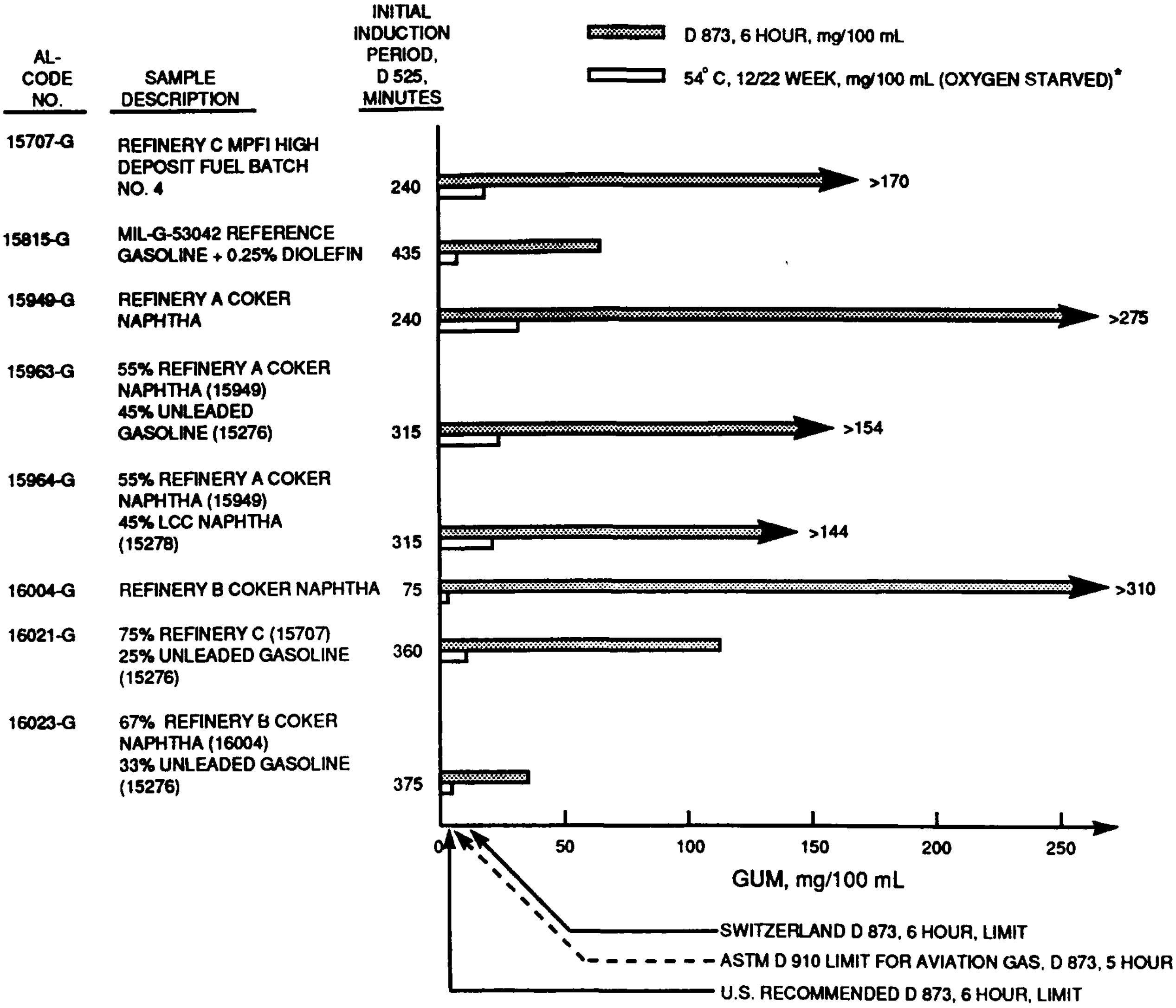
Figure 7. Phase II: gasoline blend stocks and an additional no-lead gasoline

four highest values. Note the significant reduction in D 873 gum (to 12.4 mg/100 mL) with the addition of MIL-G-53042 reference antioxidant for the coker naphtha (Code No. 15279), which had a D 525 induction period of 105 minutes before additive was added and >1770 minutes after the additive was added. The coker naphtha unwashed gum was initially 13.8 mg/100 mL. In reviewing both Fig. 7 and Appendix Fig. E-2, it is apparent that the most unstable sample was the pyrolysis naphtha. While the coker naphtha gave a high D 873 value, it did not give high gum values in 43°C, 54°C, or ambient storage. This suggests that either the reaction mechanism is very different at the D 873 test temperature of 100°C or that insufficient oxygen is available at the other test temperatures.

Since Phase II showed many gasoline blend stocks to be very stable to D 873 (both 6- and 8-hour tests), 54°C (12-week) and 43°C (24-week) storage, a number of samples in and around a D 525 induction period of 360 minutes were selected for evaluation of D 873 in Phase III. Also, in both Phases III and IV, the D 873 procedure was modified to require unwashed and washed gum values.

C. Phase III

For Phase III samples, Fig. 8 summarizes D 873 (6-hour test) gum data compared to 54°C, 12- or 22-week, storage gum data. All of these samples had D 873 gum values exceeding the ASTM D 910 limit of 6 mg/100 mL (5-hour test), the Switzerland D 873 (6-hour test) limit of



* First five samples were stored 22 weeks; other samples were stored 12 weeks.

Figure 8. Phase III: low-induction period samples

10 mg/100 mL and the U.S.-recommended D 873 (6-hour test) limit of 5 mg/100 mL. TABLE 6 summarizes the specification and surveillance limits for induction period, unwashed and existent gum, potential gum, and various gasolines. Note (in Fig. 8) that except for the Multiport Fuel Injector (MPFI) high deposit fuel (15707-G), high gum value increases were not observed for 54°C (12- or 22-week) storage. Sample No. 15707, Refinery C fuel, is the only Phase III sample that had low gum and ISD values, initially, which increased to significantly high values in 43°C, 54°C, and ambient storage. This fuel was produced as a test fuel causing high multiport fuel injector deposits. Sample Nos. 15964 (55 percent coker naphtha plus 45 percent unleaded gasoline), 15949 (Refinery A coker naphtha), and 15963 (55 percent coker naphtha plus 45 percent light catalytic cracked blend stock) had very high unwashed gum, existent gum, and ISD levels prior to storage, and did not increase in general in storage at 43°C, 54°C, or ambient. Ambient storage for these samples has now reached 208 weeks (TABLE 5 and Appendix E) and the MPFI high deposit fuel (Refinery C) shows significant increases in existent gum, peroxide number, and ISD rating. The Refinery A coker naphtha and blends with unleaded gasoline and with light catalytic cracked blend stock had high initial existent gum (>15 mg/100 mL) and ISD (>6 mg/100 mL).

D. Phase IV

For Phase IV, an effort was made to locate low-induction period gasolines at commercial fuel station outlets, which had been identified in previous surveys as having low-stability (i.e., low-induction period) gasoline. Phase IV contains low-induction period gasolines and a debutanizer bottom blend stock. Since the question had been raised about whether the laboratory gasoline stability program storage conditions represented actual storage in the U.S. and in NATO (i.e., underground with little oxygen available), it was decided to oxygen starve the 43° and 54°C storage samples. As a result, the storage samples were not aerated at each of the sampling periods [as was done in Phases I through III except the 43°C storage in Phase I, which was vented to agree with the UOP procedure (quickly abandoned in Phase II and subsequent phases because of severe evaporation)].

TABLE 6. Specification and Surveillance Limits for Various Gasolines

	Specification Limits		Specification Limits			Surveillance Limits			
						DOD		Switzerland[1]	UOP[2]
Requirement	MIL-G-5572E[3]	ASTM D 910-85	MIL-G-3056G	ASTM D 439	NATO F-57	MIL-G-5572E[3]	MIL-G-3056G	Gasoline	Gasoline
Induction Period, minutes, max	NR*	NR	480	240	360	NR	NR	360	NR
Unwashed Gum, mg/100 mL, max	NR	NR	4	NR	NR	NR	7	NR	5
Existent Gum, mg/100 mL, max	3.0	NR	NR	5	4	6.0	NR	5	5
Potential Gum, 16-hour aging, mg/100 mL, max	6.0	10	NR	NR	NR	NR	NR	NR	NR
Potential Gum, 4-hour aging, mg/100 mL, max	NR	NR	NR	NR	NR	NR	NR	NR	5
Potential Gum, 5-hour aging, mg/100 mL, max	NR	6	NR	NR	NR	NR	NR	NR	NR
Potential Gum, 6-hour aging, mg/100 mL, max	NR	NR	NR	NR	NR	NR	NR	10	NR

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* NR = No Requirement.

[1] Gartenmann, E., "Test Methods and Experience of Switzerland on Long-Term Storage Stabilities of Gasolines and Middle Distillates," Proceedings of 2nd International Conference on Long-Term Storage Stabilities of Liquid Fuels, published by Southwest Research Institute, San Antonio, TX, 1986.

[2] Schrepfer, M.W. and Stansky, C.A., "Gasoline Stability Testing and Inhibitor Application," NPRA Meeting, Paper No. FL-81-79, November 1986.

[3] Reference 29 canceled and replaced by ASTM D 910.

Two of the commercial gasolines (sample Nos. 16815-G and 16816-G) in Fig. 9 (summarizing data for Phase IV samples) contain 10-percent ethanol and had very high D 873 (6-hour test) gum values. These samples had initial induction periods of 315 and 390 minutes, respectively. The U.S. National Standard for gasoline requires a D 525 induction period minimum of 240 minutes at the refinery or at the time of transfer. Sample Nos. 16813, 16815, and 16816 had semi-high initial unwashed gum values ranging from 13.8 to 21.0 mg/100 mL (in TABLE 5). These gum values suggest that these fuels may have contained detergents, the quality and effectiveness of which are not known.

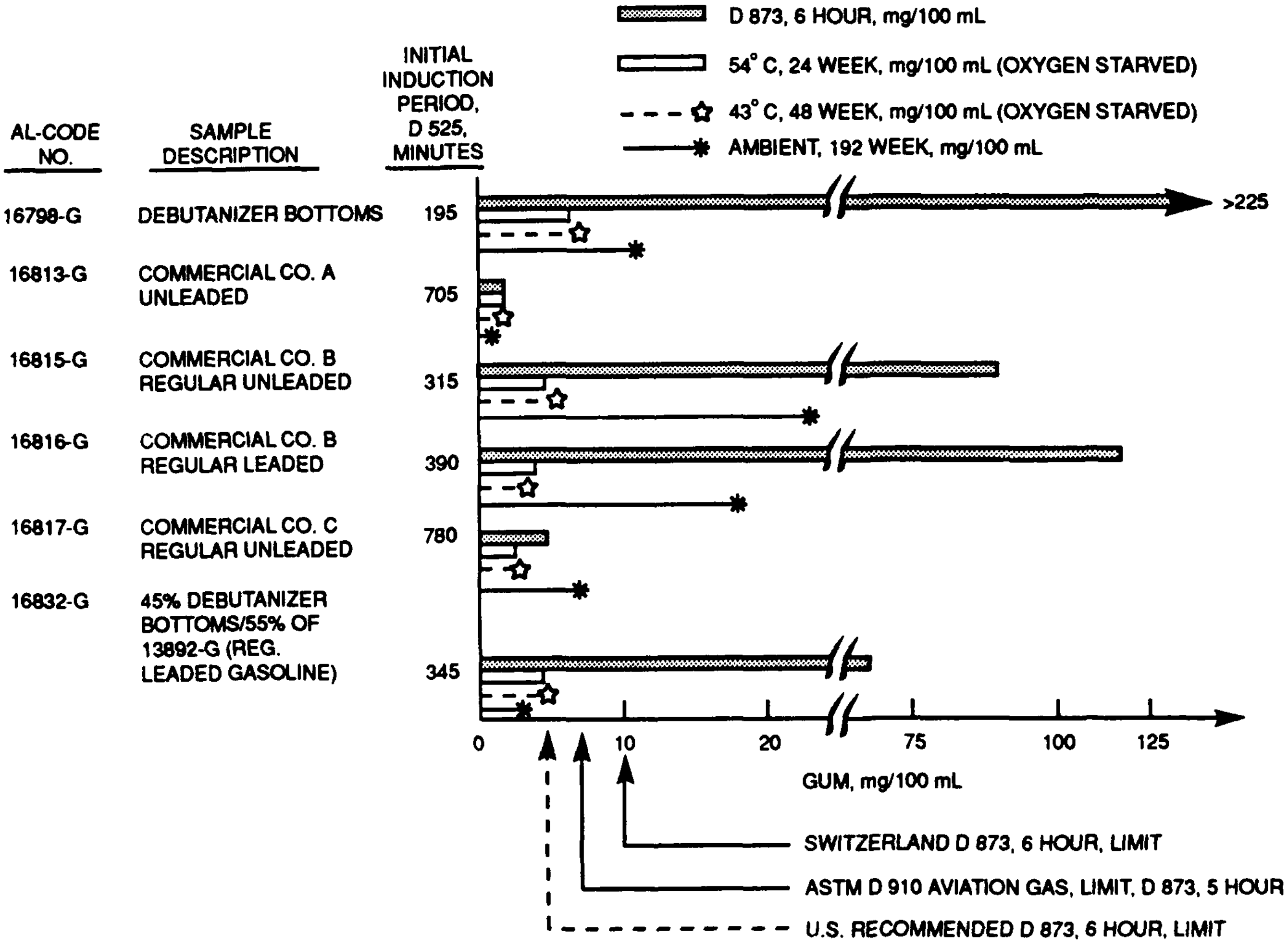

Figure 9. Phase IV: low-induction period gasolines and a blend stock

The Commercial Company B regular leaded gasoline sample (Code No. 16816) demonstrated significant existent gum and ISD rating increases during ambient storage. Data during 43° and 54°C storage were less definitive when related to D 873, 6-hour, existent gum data. Note that the 43°C and the 54°C samples were not aerated in Phase IV in order to minimize exposure to oxygen in air so as to reduce the degree of gum formation to better indicate what might occur in storage where breathing is minimized, thus reducing oxygen availability. Note also that the data suggest that 24 weeks at 53°C gives gum values very close to the 48 weeks at 43°C, a doubling of time. Also included in Fig. 9 are existent gum values at 192 weeks of ambient storage.

V. CARBURETOR AND INDUCTION SYSTEM DEPOSITING TESTS

A. Engine Evaluations

A special engine test was used to evaluate the carburetor and induction system depositing tendencies of gasolines with different induction periods. Two blends of regular leaded gasoline with LCC gasoline were prepared for this engine test, which is used primarily to screen gasoline additives developed to prevent carburetor and induction system deposits. This engine test was used here to determine if there is a significant difference in the depositing tendencies of gasolines with different levels of induction periods when stored for 4 months (equated to 16 weeks) at 43°C. The engine tests were conducted on the selected samples prior to and after they were stored for 16 weeks at 43°C, and compared to tests on the regular leaded gasoline treated in the same manner.

The engine is a standard production 4.9-liter (302 CID) Ford V/8 engine fitted with a modified intake system that permits dual carburetor operation, through which two different fuels can be metered. Preweighed aluminum sleeves in the carburetors collect throat deposits, while preweighed heated aluminum tubes below the carburetors collect deposits representative of intake valve-tulip deposits. The test is conducted on two fuels at the same time, each fuel passing through a set of carburetor sleeve-heated tube and then mingling before entering the combustion chambers. The test is run for 6 hours and consumes about 5 gallons of each test fuel. This test is described in detail in Interim Report AFLRL No. 43, "Development of a Bench Procedure for Evaluating the Effectiveness of Dispersant-Detergent Gasoline Additives--Phase I.(31)

At the completion of the test, the preweighed carburetor sleeves and tubes are removed, placed in a desiccator to cool and dry, weighed and photographed. They are then washed with a hydrocarbon solvent to displace residual gasoline dyes and additives, dried, and again weighed and photographed. Thus, the masses of any deposits formed are recorded. A satisfactory level of deposits for either the carburetor sleeve or the metal tube is 2.0 mg maximum.

Data for the samples evaluated in these engine tests, before and after 16-weeks storage at 43°C, are shown in TABLE 7. In preparing these blends, the goal was to have their induction periods at approximately 360 and 480 minutes.

The results of the engine tests, conducted on the three gasolines before and after the aging period, are presented in TABLE 8. The data show that all the gasolines had satisfactory levels of deposits before aging; however, after the 16-week aging period, the two gasoline blends containing LCC had tube deposits above the acceptable level. The gasoline (38 vol% LCC, 62 vol% RLG) with lower induction period (450 minutes) had the highest level of tube deposits after the storage period.

The data presented here are not sufficient for firm conclusions, but imply that gasolines with low-induction periods that have been stored for lengthy periods may cause unacceptable levels of engine deposits.

B. Laboratory Bench Test

The tendency of motor gasolines to form deposits on the intake valve and port surfaces of spark-ignition engines can be evaluated by a bench apparatus developed for the U.S. Army.(12) The apparatus consists of a carbureted fuel-air system that sprays the test fluid on a heated deposit collecting tube at a 2.0 mL/minute rate, as per Federal Test Method Standard 791C, Method

TABLE 7. Samples Used in Carburetor and Induction System Depositing Test

Sample Description	Induction Period, D 525, minutes	Unwashed Gum, mg/100 mL	Existent Gum, mg/100 mL	D 873, Potential Gum, mg/100 mL, 4 hr	Stored at 43°C - 16 weeks		
					Unwashed Gum, mg/100 mL	Existent Gum, mg/100 mL	ISD, mg/100 mL
AL-13893-G Regular Leaded Gasoline	>960	0.3	0.3	2.0	0.2	0.0	0.1
AL-14825-G 30 vol% LCC, 70 vol% Regular Leaded Gasoline	>960*	3.0	0.6	7.6**	4.9	0.6	0.4
AL-14824-G 38 vol% LCC, 62 vol% Regular Leaded Gasoline	450	4.4	1.2	16.9**	7.7	1.3	0.6

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* Test showed 20 psi pressure drop in 540 minutes.

** Average of duplicate determinations.

TABLE 8. Engine Test Data

Sample Description	Carburetor Sleeve Deposits, mg† Before Storage	Carburetor Sleeve Deposits, mg† After Storage	Tube Deposits, mg† Before Storage	Tube Deposits, mg† After Storage
AL-13893-G Regular Leaded Gasoline (>6030 Induction Period)	0.9 to 1.4* (1.5)**	0.5	0.9 to 1.1* (0.7)**	1.2
AL-14825-G 30 vol% LCC, 70 vol% Regular Leaded Gasoline (>960 Induction Period)	0.2	0.2	1.1	2.7
AL-14824-G 38 vol% LCC, 62 vol% Regular Leaded Gasoline (450 Induction Period)	0.6	1.5	1.3	3.7

† A satisfactory level of deposits for either the carburetor sleeve or the metal tube is 2.0 mg maximum.

* Two tests were conducted with AL-13893-G before storage at 43°C.

** This test also was with AL-13893-G before storage at 43°C.

500.1, "Induction System Deposit (ISD) Rating." Correlations between this test method and both fleet and engine tests (including the split carburetor engine test in section "A" above) have indicated that ISD values of 2.0 mg/100 mL or higher by Federal Test Method 500.1 are deleterious to engine valve operation.

Fig. 10 is a plot of ISD ratings versus existent gum for samples stored at 43° and 54°C for maximum periods of time. In the plot and statistical analyses of selected properties, three Phase I samples with D 381, Existent Gum values of 103 mg/100 mL, 264 mg/100 mL, and

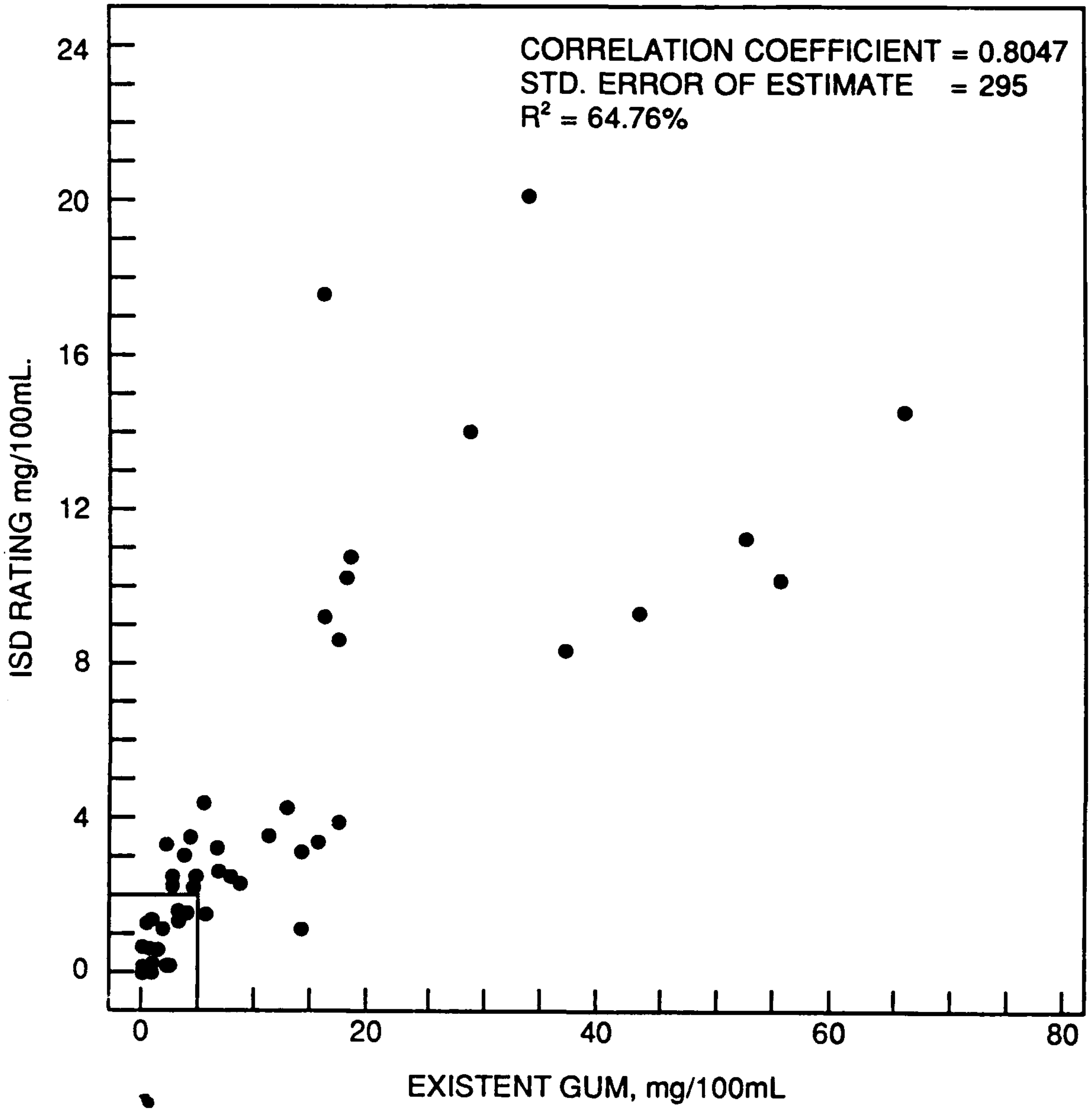

Figure 10. Existent gum versus ISD rating--all phases at 43° and 54°C
(After maximum storage time; data from Appendix D)

262 mg/100 mL at 43°C as well as one Phase II sample with an ISD rating of 119 mg/100 mL at 43°C and 302 mg/100 mL at 54°C were not used for the chart in Fig. 8, because of their magnitude compared to the bulk of the data that were used.

While the correlation coefficient of 0.8047 is substantial, note that when existent gum values exceed about 5 mg/100 mL, ISD ratings exceed 2 mg/100 mL. ISD ratings of 2 mg/100 mL or greater are considered to be unacceptable. This rating supports the recommendation shown in

Figs. 6 through 9, for a limit of 5 mg/100 mL maximum D 873 (6-hour test) value, to assure a gum value of no more than 5 mg/100 mL in 4-year ambient (13°C) storage.

VI. SUMMARY

For low existent gum fuels similar to those used in Phase I, earlier work has tended to show that existent gum increases in 100°C tests are essentially equal to unwashed gum increases.(8) Hence, in Phases I and II, the modified D 873 test only determined unwashed gum. Comparison of unwashed and existent gum in samples stored at 43° and 54°C suggest similar unwashed and existent gum values. Note also when comparing 43°C data that for Phase I, these containers were vented (which resulted in high evaporation of sample with time). Both 43° and 54°C storage utilized closed (nonvented) containers in Phases II through IV. In order to evaluate modern commercial gasolines, existent as well as unwashed gum was measured in Phases III and IV in the modified D 873 test (Appendix B) since modern gasolines tend to have high unwashed gums due to the presence of deposit modifiers or detergent additive packages.

TABLE 9 groups ambient storage and modified D 873 data for test samples, which were essentially finished gasolines. Based on this limited data, it was recommended that the limit for 6-hour D 873 be 5 mg/100 mL, to achieve a <5 mg/100 mL existent gum level in 4-year ambient (25°C, vented store room) storage. In a 1988 paper (32) on this work entitled "Evaluation of Motor Gasoline Stability," it was stated:

> "Results to date confirm the findings of earlier researchers that ASTM D 525 is not viable as a predictive device by virtue of a low coefficient of determination between induction period and gum formed in storage at 43°C for periods up to 1 year. It is recognized, however, that ASTM D 525 is not likely to be abandoned as a specification stability test. Based upon the data generated to date under the four phases of this storage stability program including supporting data obtained from literature sources and current surveillance information on both military and

TABLE 9. Summary of D 873 and Ambient Storage Data for Gasoline Samples in Phases I Through IV

AL-Code No.	Sample Description	4-Hour Modified D 873 Gum, mg/100 mL			6-Hour (or Other) Modified D 873 Gum, mg/100 mL		D 381, Gum, mg/100 mL Existent		
		Unwashed		Existent	Unwashed	Existent	Ambient Storage		
		Initial	4 hr				0 wk	176 wk	208 wk
Phase I									
14389-G	50% LCC, 50% Regular Leaded Gasoline	5.5	8.3	--	48 (4.8 hr)	--	0.2	22	76
14390-G	40% LCC, 60% Regular Leaded Gasoline	5.3	4.7	--	33	--	1.1	40	42
14391-G	35% LCC, 65% Regular Leaded Gasoline	3.9	5.2	--	16	--	0.0	15	25
14392-G	30% LCC, 70% Regular Leaded Gasoline	4.7	5.3	--	17	--	0.6	4.5	8.5
13893-G	100% Regular Leaded Gasoline	0.6	2.0	--	1.5	--	0.5	1.2	2.4
Phase II									
15276-G	No-Lead Gasoline	1.2	2.4	--	3.5	--	0.4	1.6	2.1
Phase III									
15707-G	Refinery C MPFI High Deposit Fuel Batch No. 4	7.3	174	169	--	(>170)	4.3	204	449
16021-G	75% RefineryC (15707) + Unleaded Gasoline (15276)	8.8	30	18	125	112	4.5	16	10
Phase IV									
16813-G	Commercial Co. A Unleaded	13.8	16	0.4	15	0.3	0.0	0.3	--
16815-G	Commercial Co. B Regular Unleaded	21.0	29	16	94	88	0.0	11.9	--
16816-G	Commercial Co. B Regular Leaded	14.4	52	36	154	116	0.1	40*	--
16817-G	Commercial Co. C Regular Unleaded	5.2	5.3	2.5	7.5	4.5	0.0	5.3	--

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* Value is extrapolated.

> industry practices, the method to be adopted for evaluating stability of commercial/military motor gasoline will consist of the modified ASTM D 873 Method using a 6-hour aging existent gum maximum limit of 20 mg/100 mL. The ability of this test to distinguish between stable and unstable low induction period fuels and/or components is discussed."

The 6-hour D 873 value of 20 mg/100 mL seemed acceptable when reviewing the data in TABLES 3, 4, and 9 and the data in Fig. 11 in considering storage in NATO at 10° ± 6°C. However, when considering the gum and ISD data in Fig. 8, it was decided that existent gum values above 5 mg/100 mL could not be acceptable as these correlated to unacceptably high ISD values.

Hence, the recommendation for the 5 mg/100 mL limit for 6-hour D 873 (modified) was here recommended (although this may be too demanding for fuel to be stored at low temperatures in NATO).

By minimizing availability of oxygen in air, storage periods can be greatly extended. Using this approach, very unstable gasolines can be stored in oxygen free containers indefinitely without deterioration. These same fuels would deteriorate rapidly if stored in 1960 technology vehicle fuel systems in warm ambient areas. Modern vehicles tend to use nonbreathing multiport fuel injected systems to minimize vehicle volatile emissions as well as to provide for computer-controlled fuel delivery to maximize performance and minimize exhaust emissions.

To demonstrate the effect of oxygen starvation, the 43° and 54°C storage of Phase IV samples was without aeration of samples at the sampling periods. Using this existent gum data summarized graphically in Appendix E, the time to reach 5 mg/100 mL was estimated by extrapolation and summarized in TABLE 10. Using the multiplication factors from TABLE 2 for Methods A and B, storage time at lower temperatures was calculated from the extrapolated storage times at 43° and 54°C. The more conservative (lower numerical multiplication values)

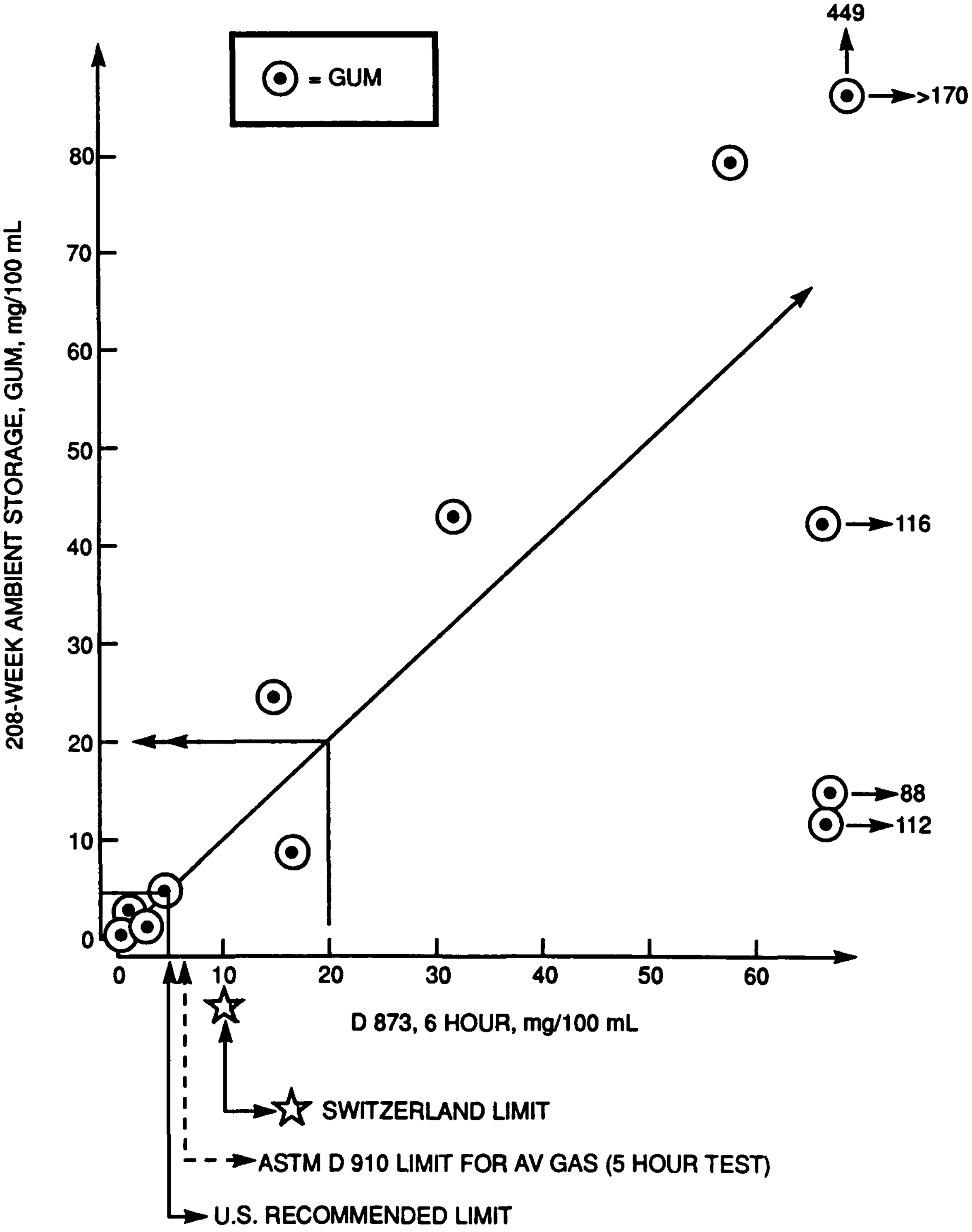

Figure 11. Gum formed during ambient storage and 6-hour D 873 test

TABLE 10. Prediction of Storage Time at Lower Temperatures Using 43° and 54°C Data in Phase IV

AL-Code No.	Sample Description	43°C Storage Temperature Data: Time to Reach 5 mg/100 mL, years	43°C Storage Temperature Data: Predicted Time in Storage*, years, at			54°C Storage Temperature Data: Time to Reach 5 mg/100 mL, years	54°C Storage Temperature Data: Predicted Time in Storage*, years, at			
			33°C	23°C	13°C		43°C	33°C	23°C	13°C
			Method A							
Phase IV										
16798-G	Debutanizer Bottoms	0.9	1.8	3.7	7.4	0.05	0.11	0.22	0.4	0.9
16813-G	Commercial Co. A Unleaded	1.9	3.8	7.7	15.4	0.7	1.4	2.8	6	11
16815-G	Commercial Co. B Regular Unleaded	0.9	1.8	3.7	7.4	0.5	0.9	1.8	4	7
16816-G	Commercial Co. B Regular Leaded	1.2	2.5	4.9	9.8	0.7	1.4	2.8	6	11
16817-G	Commercial Co. C Regular Unleaded	1.5	3.1	6.2	12.3	0.15	0.3	0.6	1.2	2.5
16832-G	45% Debutanizer Bottoms/55% of 13892-G (Reg. Leaded Gasoline)	0.9	1.8	3.7	7.4	0.33	0.7	1.4	3	5
			Method B							
Phase IV										
16798-G	Debutanizer Bottoms	0.9	2.7	8.3	29	0.05	0.2	0.5	1.4	5
16813-G	Commercial Co. A Unleaded	1.9	5.6	17.3	60	0.7	2.1	5.5	17	57
16815-G	Commercial Co. B Regular Unleaded	0.9	2.7	8.3	29	0.5	1.4	3.7	11.5	38
16816-G	Commercial Co. B Regular Leaded	1.2	3.6	11	38	0.7	2.1	5.5	17	57
16817-G	Commercial Co. C Regular Unleaded	1.5	4.5	13.8	48	0.15	0.5	1.2	3.8	13
16832-G	45% Debutanizer Bottoms/55% of 13892-G (Reg. Leaded Gasoline)	0.9	2.7	8.3	29	0.33	1	2.6	8	27

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* Assumes same oxygen starved environment, constant temperature.

predictive method (Method A) gave storage times greater than 7 years at 13°C (from the 43°C data) and greater than 1 year (from the 54°C data). Using the Method B (Arrhenius equation), the minimum storage time at 13°C was 5 years.

Modification of D 873 (as shown in Appendix B) for use in this program could have been to simply add automotive gasoline to TABLE 2 of D 873 as done here in TABLE 11. As can be seen in TABLE 11, D 873 currently applies to aviation reciprocating engine fuel (aviation gasoline) and aviation turbine fuel, but not to automotive gasoline.

TABLE 11. Modified TABLE 2 (Aging Characteristics) of D 873

Aging Characteristic to Be Reported	Residue Fractions to Be Combined	
	Aviation Reciprocating Engine Fuel	Aviation Turbine Fuel
Potential gum, mg/100 mL	sum of insoluble gum (Note 2) and soluble gum (B + C)	.....
Precipitate, mg/100 mL	precipitate (A) if required	.....
Total potential residue, mg/100 mL	.....	sum of precipitate A (if required) insoluble gum B and soluble gum C (A + B + C)
	Automotive Gasoline	
Potential unwashed gum, mg/100 mL	soluble gum (C)	
Potential existent gum, mg/100 mL	washed soluble gum (C)	

VII. CONCLUSIONS AND RECOMMENDATIONS

While it is recognized that very few commercial gasolines are likely to have low (360 to 480 minute) induction periods, a test is needed to screen out storage unstable gasoline from use in long-term strategic storage. The aging test results obtained during this program have demonstrated the proposed storage stability test, ASTM D 873, Standard Test Method for Oxidation Stability of Aviation Fuels (Potential Residue Method), with a slight modification to give unwashed and existent gum values, to be acceptable in (evaluating) predicting motor gasoline stability. This method has been shown to correlate gasoline stability at 100°C and ambient (25°C average) conditions by observing existent gum formed in gasoline stored up to 4 years in ambient conditions. Based on the data generated under the four phases of this storage stability program, including supporting data obtained from literature sources and current surveillance information on both military and industry practices (see TABLE 6), the method recommended for evaluating stability of commercial/military gasoline is ASTM D 873 with a 6-hour aging period and absolute maximum existent gum limit of 5 mg/100 mL or, if this limit is too restrictive, a gain of 5 mg/100 mL. This limit represents a compromise in (assessing) predicting storage stability for a 4-year period for military gasolines, i.e., F-46 gasolines have been required to meet both an ASTM D 525 limit of 480 minutes minimum and an ASTM D 381 unwashed gum limit of 4 mg/100 mL maximum. It is recommended that commercial/military gasolines be required to meet an ASTM D 873 existent gum limit of 5 mg/100 mL maximum after a 6-hour aging period and an ASTM D 381 existent gum limit of 4 mg/100 mL maximum. Use of modern detergent additives in commercial gasolines may readily reduce D 873 washed gum values (as they do D 381 existent gum values) but not accurately relate to vehicle fuel system deposit propensity. Insufficient data exist for modern formulated gasolines to state that D 381 is biased from correlating with engine deposition reality, except to say that modern (deposit-forming) gasolines requiring the use of modern technology detergent additive packages have not been accurately evaluated by D 381. Thus, it is reasonable to conclude that D 873 will not accurately evaluate the storage stability of these gasolines. For modern detergent formulated gasolines, it is recommended that the D 873 stability methodology be restricted to refinery gasoline blends not containing modern detergents and that larger scale detergent additized gasoline storage stability evaluations including accelerated aging correlation to modern bench injector and valve deposition tests be performed. This conclusion and recommendation is further supported by the data and discussion in Appendix A. Minimization of storage temperatures and availability of oxygen can greatly reduce deterioration of unstable gasoline during storage and in vehicle systems prior to consumption.

VIII. LIST OF REFERENCES

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LIST OF ABBREVIATIONS

AFLRL	- U.S. Army Fuels and Lubricants Research Laboratory
Alky	- Alkylate
AO	- Antioxidant
ASTM	- American Society for Testing and Materials
bbl	- Barrel
BFLRF	- Belvoir Fuels and Lubricants Research Facility (SwRI)
Belvoir RDE Center	- U.S. Army Belvoir Research, Development and Engineering Center
CEPS	- Central European Pipeline System
CEOA	- Central European Operating Agency
CID	- Cubic Inch Diameter
C.N.	- Coker Naphtha
CRC	- Coordinating Research Council
EP	- End Point
FIA	- Fluorescent Indicator Absorption
FTM	- Federal Test Method
G	- Gasoline
HCC	- Heavy Catalytic Cracked
HC	- Hydrocracked
HSR	- Heavy Straight Run
IBP	- Initial Boiling Point
ISD	- Induction System Deposit
L	- Liter
lb	- Pound
LCC	- Light Catalytic Cracked
Ld.	- Leaded
LSR	- Light Straight Run
mL	- Milliliter
mg	- Milligram
MON	- Motor Octane Number
MPFI	- Multiport Fuel Injector
NATO	- North Atlantic Treaty Organization
NIPER	- National Institute for Petroleum and Energy Research

LIST OF ABBREVIATIONS (Cont'd)

Ref	- Referee Blend
RLG	- Regular Leaded Gasoline
RON	- Research Octane Number
RVP	- Reid Vapor Pressure
SwRI	- Southwest Research Institute
TX	- Texas
U. Ld.	- Unleaded
UOP	- Universal Oil Production

GLOSSARY

Alkylation - Denotes a process to produce a high octane gasoline blending component by combining light olefins with isoparaffins. (Alkylate is the main product from alkylation.)

Antioxidant - An additive to inhibit oxidation.

Aromatics, ASTM D 1319 - The volume percent of monocyclic and polycyclic aromatics, plus aromatic olefins, plus some dienes, plus some compounds containing sulfur, nitrogen and oxygen atoms.

ASTM D 86 - Standard Test Method for Distillation of Petroleum Products

ASTM D 156 - Standard Test Method for Saybolt Color of Petroleum Products (Saybolt Chromometer Method)

ASTM D 323 - Standard Test Method for Vapor Pressure of Petroleum Products (Reid Method)

ASTM D 381 - Standard Test Method for Existent Gum in Fuels by Jet Evaporation

ASTM D 439 - Standard Specification for Automotive Gasoline (Intent to Withdraw)

ASTM D 525 - Standard Test Method for Oxidation Stability of Gasoline (Induction Period Method)

ASTM D 873 - Standard Test Method for Oxidation Stability of Aviation Fuels (Potential Residue Method)

ASTM D 873, Modified - A Tentative Method for Oxidation Stability of Motor Gasolines (Total Potential Gum Method)

ASTM D 910 - Standard Specification for Aviation Gasolines

ASTM D 1298 - Standard Practice for Density, Relative Density (Specific Gravity), or API Gravity of Crude Petroleum and Liquid Petroleum Products by Hydrometer Method

ASTM D 1319 - Standard Test Method for Hydrocarbon Types in Liquid Petroleum Products by Fluorescent Indicator Adsorption

ASTM D 1500 - Standard Test Method for ASTM Color of Petroleum Products (ASTM Color Scale)

ASTM D 2699 - Standard Test Method for Knock Characteristics of Motor Fuels by The Research Method

GLOSSARY (Cont'd)

ASTM D 2700 - Standard Test Method for Knock Characteristics of Motor Aviation Fuels by The Motor Method

ASTM D 4814 - Standard Specification for Automotive Spark-Ignition Engine Fuel (Supersedes ASTM D 439)

Break Point, ASTM D 525 - The point in the pressure-time curve that is preceded by a pressure drop of exactly 2 psi (13.8 kPa) within 15 minutes and succeeded by a drop of not less than 2 psi in 15 minutes.

Catalytic Cracking - The main process used to convert more of a barrel of crude oil into ligher mobility fuels. A catalyst is used to accelerate the cracking of the heavy portions.

Coker Naphtha - Product in the gasoline boiling range of 38° to 204°C, produced from coking of heavy oils.

Corrosion Inhibitor - An additive that imparts anti-rust properties to gasoline.

Cracking - The breaking down of higher molecular-weight hydrocarbons to lighter components by the application of heat.

Debutanizer Bottoms - Product of catalytic cracking after separation of butane and butylene fraction as the overhead product.

Distillation, ASTM D 86 - A measure of volatility characteristics of hydrocarbons; vaporization of a liquid and its subsequent condensation in a separate container.

Existent Gum, ASTM D 381 - The heptane-insoluble portion of the evaporation residue of motor gasoline.

Existent Gum, ASTM D 873 (Modified) - The evaporation residue of the heptane-insoluble portion of the total unwashed gum.

Federal Test Method Standard No. 791 - Lubricants, Liquid Fuels, and Related Products; Methods of Testing

Filterable Precipitate, U.S. Bureau of Mines - Sediment and suspended material in the aged fuel obtained by filtration.

Gum - Nonvolatile insoluble deposits formed during fuel deterioration.

Heavy Catalytic Cracked Naphtha - High end of the catalytic gasoline boiling range.

Heavy Straight Run Naphtha - Consists of a fraction with a boiling range between 88° and 204°C.

Heptane Wash - To extract a sample with heptane to determine the heptane-insoluble portion of a sample.

Hydrocracking - Process for cracking at high pressure in the presence of hydrogen and catalyst. This process is used to upgrade the heavier portions of the crude to lighter fuel oils and gasoline.

Induction Period, ASTM D 525 - The time elapsed between the placing of the bomb in the bath and the break point at 100°C.

Induction System Deposit (ISD) Index, Federal Test Method Standard No. 791C, 500.1 - Weight gain of the deposit tube obtained from 100 mL of gasoline.

Insoluble Gum, ASTM D 873 - Deposit adhering to the glass sample container after removal of the aged fuel, precipitate, and soluble gum. Insoluble gum is obtained by measuring the increase in weight of the glass sample container.

Light Catalytic Cracked Naphtha - Light end of catalytic gasoline boiling range.

Light Straight Run Naphtha - Consists of the C_5-88°C fraction of the naphtha cuts from the crude still.

Metal Deactivator - An additive to inhibit gum formation catalyzed by metals.

Naphtha - Refers to unrefined, partly refined, or refined petroleum products that distill between 38° and 238°C.

Octane Number - (Research Octane No. + Motor Octane No.) divided by 2 - A term used to indicate numerically the knock-resistance of a fuel for spark-ignition engines.

Olefins, ASTM D 1319 - The volume percent of alkenes, plus cycloalkenes, plus some dienes.

Oxidation Inhibitor - An additive to prevent the formation of gums and peroxides.

Peroxide Number, UOP 33-82 - The magnitude of the peroxide number indicates the quantity of oxidizing constituents present.

Potential Gum, ASTM D 873 - Sum of the soluble and insoluble gum.

Precipitate - Sediment and suspended material physically separated from a solution.

GLOSSARY (Cont'd)

Precipitate, ASTM D 873 - Sediment and suspended material in the aged fuel obtained by filtering the aged fuel and washings from the glass sample container.

Pyrolysis Naphtha - A product of thermal cracking for the production of ethylene resulting from polymerization of smaller molecules. Unstable product containing high concentrations of olefins and aromatics.

Raffinate - The insoluble fraction recovered from an extraction process.

Reformate - A reformed naphtha, which is upgraded in octane by means of catalytic reforming to convert cycloparaffins to aromatics.

Residue - Material remaining after evaporation, distillation, filtration, or extraction.

Saturates, ASTM D 1319 - The volume percent of alkanes plus cycloalkanes.

Soluble Gum, ASTM D 873 - Deterioration products present at the end of a specific aging period. These deterioration products exist in solution in the aged fuel and as the toluene-acetone soluble portion of the deposit on the glass sample container. The soluble gum is obtained as a nonvolatile residue by evaporating the aged fuel and the toluene-acetone washings from the glass sample container.

Total Potential Residue, ASTM D 873 - Sum of the potential gum and the precipitate.

Total Unwashed (Potential) Gum, ASTM D 873 (Modified) - Deterioration products present at the end of a specific aging period. These deterioration products are collected from the aged fuel and from the toluene-acetone soluble portion of the deposit on the glass sample container.

Unwashed Gum, ASTM D 381 - The evaporation residue of motor gasoline consisting of existent gum and nonvolatile additive components.

Wall-Adhered Insoluble Gum, U.S. Bureau of Mines - The toluene-acetone soluble portion of the deposit on the glass sample container.

Washed Gum, ASTM D 381 - Heptane-insoluble portion of the evaporation residue of motor gasoline (existent gum).

APPENDIX A

Summary of Oxidation Stability and Potential Gum for Typical Civilian Gasolines Transported by CEPS and F-46 Gasolines Stored by CEPS

APPENDIX A

Summary of Oxidation Stability and Potential Gum for Typical Civilian Gasolines Transported by CEPS and F-46 Gasolines Stored by CEPS

A 1983 Central European Operating Agency (CEOA) stability survey of F-46 gasolines (in storage) and commercial gasolines was provided by CEOA.

TABLE A-1 presents stability characteristics of "typical civilian gasolines" transported by Central European Pipeline System (CEPS) in 1983.

If one looks at the total potential gum (unwashed) (in TABLE A-1) compared to the D 381 unwashed gum, values of 1.2 and 4.6 compared to 12.6 and 117.0 mg/100 mL for sample Nos. 4 and 12, respectively, with low D 525 induction periods (600 and 555 minutes); these two gasolines would appear to be very unstable gasolines not desirable for long-term storage.

TABLE A-2 presents selected stability data for F-46 military gasolines in storage in CEPS provided by the Central European Operating Agency (CEOA). Of 37 fuels received in 1983, followup analyses within 1 year (or less) showed 12 to be outside the original limits for procurement under NATO Code No. F-46 (4.0 mg/100 mL unwashed gum). Also, 27 percent of all fuels listed in TABLE A-2 were, when tested, outside the gum limits for use in combat vehicles or stationary engines (based on U.S. Army surveillance limits). F-46 allows use of detergents and top cylinder oils, which may account for these high unwashed gums in TABLE A-2. A gum specification for procurement is thus shown to be inadequate protection against fuel instability according to U.S. Army requirements. Note also in TABLE A-2, only one of the 59 samples had a D 525 induction period of <600 minutes and it was 555 minutes (which is appreciably greater than the F-57 360 minute, minimum, limit.)

TABLE A-1. Stability Characteristics of Typical Civilian Gasolines Transported by CEPS in 1983

Sample No.	Country	Identification	Date	D 525, minutes*	D 381 Gum, mg/100 mL Unwashed	D 381 Gum, mg/100 mL Existent	D 873* Total Potential Gum, mg/100 mL
1	France	Super	06-10-83	>1440	4.0	1.4	7.1
2	France	Super	03-11-83	>1440	3.8	1.2	7.5
3	France	Super	07-11-83	>1440	3.0	1.2	5.9
4	France	ICCG	05-10-83	600	1.2	0.8	12.6
5	France	Super	08-20-83	1750	5.0	3.8	8.6
6	France	Regular	08-18-83	>6000	1.3	0.9	3.6
7	Belgium	Super	12-21-83	1740	2.6	1.0	7.0
8	Belgium	Super	03-10-83	1290	1.4	0.4	4.1
9	Belgium	Super	02-09-83	1335	0.4	0.2	4.0
10	Netherlands	Super	06-10-83	>1500	1.6	0.4	3.8
11	Netherlands	Regular	11-16-83	>1500	1.2	0.8	4.6
12	Federal Republic of Germany	Regular	12-21-83	555	4.6	0.7	117.0
13	Federal Republic of Germany	Regular	12-21-83	555	31.1	2.9	38.7

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* Time at which the breakpoint was reached and then submitted to D 873 gum determinations. The ">" signifies the breakpoint was greater than the time at which the test was stopped.

TABLE A-2. Stability Characteristics of F-46 Gasolines

Source: Central European Operating Agency Survey Data; Analyses performed in summer/fall 1983.

Note: Gum values shown are mg gum per 100 mL fuel.

Depot	Receipt Date	D 525 Minutes	D 381 Gums; Unwashed*		8-hour Gum**
			Unwashed*	Existent	
DBAD	10-12-79	2130	10.0	1.8	11.0
DWKD	10-22-80	2000	10.6	2.3	24.5
DWKD	10-22-80	2265	20.9	1.1	32.8
DBFD	03-18-81	1980	16.9	4.4	24.1
BGAD	09-//-81	>4500	7.2	3.2	8.5
BGAD	09-//-81	5355	5.4	2.2	8.2
DHUD	09-18-81	765	4.2	0.8	15.6
DHUD	09-18-81	945	7.5	2.2	18.3
DHUD	12-21-81	850	16.4	3.5	18.6
FLGK	01-12-82	>1440	2.6	1.5	5.0
FLGK	01-13-82	>1440	2.8	1.8	6.8
NHKD	04-16-82	>1500	3.4	2.0	10.8
DWKD	06-04-82	1650	6.3	1.4	8.9
DHUD	06-08-82	960	8.5	1.8	18.5
DHUD	06-08-82	960	6.0	1.8	14.9
DWKD	06-14-82	2265	17.3	0.8	39.7
DHBD	06-30-82	810	2.5	2.0	5.8
NHKD	09-11-82	>1500	2.8	2.0	7.2
DHBD	09-28-82	945	19.8	1.0	36.3
DHBD	09-29-82	930	13.9	1.0	19.3
DGBD	10-03-82	1635	3.7	1.0	12.6
DGBD	10-06-82	1020	22.1	0.6	52.6
BSCD	02-//-83	5195	2.2	1.6	4.1
NWOD	02-17-83	>1500	0.6	0.4	6.4
BGLD	03-//-83	3135	3.8	0.8	9.2
DMLD	03-08-83	2865	11.2	1.8	15.2
DMLD	03-08-83	2475	7.0	1.5	15.6
FPBD	04-28-83	990	4.7	2.3	8.9
NMAD	05-15-83	>1500	3.4	0.6	6.4
NKLD	06-01-83	>1500	1.2	0.6	3.0
DKKD	06-16-83	1485	2.2	1.0	13.2
DKKD	06-16-83	1515	2.4	0.6	6.4
NMAD	06-20-83	>1500	2.0	0.4	4.4
DTUD	06-21-83	1785	23.9	1.7	22.5
DTUD	06-21-83	1785	6.3	2.5	14.1
NHKD	06-23-83	>1500	2.0	1.8	4.2
DAAD	06-28-83	1095	12.7	1.3	13.4
BSVD	07-//-83	1740	3.4	1.8	7.1
DFUD	07-09-83	1770	3.5	2.0	15.6
DHUD	07-25-83	850	3.6	1.0	13.2
BGLD	08-//-83	3300	2.8	1.2	6.6
NPKD	08-21-83	>1500	0.6	0.4	3.4
FLGK	9-6/7-83	>1440	1.6	1.2	4.7
FLGK	09-07-83	>1440	2.2	1.3	7.4
DZWD	09-07-83	660	3.3	1.9	14.2
DZMD	09-07-83	660	2.9	1.4	18.5
DFUD	09-24-83	1770	4.4	1.0	19.6
DBAD	09-28-83	2100	3.8	1.2	7.5
DOBD	10-19-83	2170	7.7	2.8	9.4
DBAD	10-25-83	2650	2.8	1.0	6.5
DBAD	10-26-83	2190	3.8	1.0	7.7
DABD	11-14-83	600	15.7	2.2	20.7
DABD	11-14-83	585	11.6	3.8	20.8
DHUD	11-14-83	1050	61.4	2.7	69.7
DPSD	12-06-83	615	3.0	1.0	13.8
DPSD	12-08-83	600	3.4	1.0	15.9
DBKD	12-09-83	555	11.2	1.0	38.0
DBKD	12-16-83	630	2.2	0.6	13.0
DBKD	12-16-83	630	3.0	0.8	13.0

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* The procurement limit under MIL-G-3056, F-46, and F-47 is 4 mg/100 mL.

** ASTM D 873.

APPENDIX B

Potential Gum Residue Method and Sample Handling Procedure

BELVOIR FUELS AND LUBRICANTS RESEARCH FACILITY (SwRI)
6220 CULEBRA ROAD—P.O.DRAWER 28510 PH:512-684-5111 SAN ANTONIO,TEXAS 78284

BFLRF

File: 02-1955-166
21 December 1989

Commander
U.S. Army Belvoir Research, Development and Engineering Center
Attn: STRBE-VF, Mr. M.E. LePera
Fort Belvoir, Virginia 22060-5606

Subject: **Potential Gum Residue Method and Sample Handling Procedure**

Reference: Belvoir RDE Center, STRBE-VF, ACTION LIST From 15th GFWP Meeting of AC/112 (WG/4)

Dear Sir:

1. Enclosure No. 1 is the "Tentative Method for Oxidation Stability of Motor Gasolines." This method uses an accelerated aging period of 6 hours and both unwashed and existent gum are reported. This method differs from ASTM D 873 in that any precipitate (if present) is not measured separately by filtration and insoluble gum, as defined in D 873, is not measured. For the purposes of evaluating this method, it is recommended that neat (unaged) fuel be evaluated for unwashed and (washed) existent gum by ASTM D 381. Anticipated precision of this potential gum method (Enclosure No. 1) is the same as that reported for aviation reciprocating engine fuel in ASTM D 873, i.e., the results of two determinations on the same sample should not differ by more than the following amounts:

	Repeatability	Reproducibility
Potential gum, mg/100 mL:		
Up to 5	2	3
Over 5 to 10	3	4
Over 10 to 20	4	6

2. ASTM D 4057 (Standard Practice for Manual Sampling of Petroleum and Petroleum Products) states under the section on "Oxidation Stability":

10.4.1 When sampling products that are to be tested for oxidation stability in accordance with Method D 525, Method D 873, or by equivalent methods, observe the following precautions and instructions:

10.4.1.1 *Precautions*--Very small amounts (as low as 0.001 %) of some materials, such as inhibitors, have a considerable effect upon oxidation stability tests. Avoid contamination and exposure to light while taking and handling samples. To prevent undue agitation with air which promotes oxidation, do not pour, shake, or stir samples to any greater extent than necessary. Never expose them to temperatures above those necessitated by atmospheric conditions.

10.4.1.2 *Sample Containers*--Use only brown glass or wrapped clear glass bottles as containers, since it is difficult to make certain that cans are free of contaminants, such as rust and soldering flux. Clean the bottles by the procedure described in 8.1.3.3 and, if possible, finish with a cleaning solution of sulfuric acid and potassium dichromate. Rinse thoroughly with distilled water, dry, and protect the bottles from dust and dirt.

10.4.1.3 *Sampling*--An all-levels sample obtained by the bottle procedure, 8.2.3.1, is recommended because the sample is taken directly in the bottle. This reduces the possibility of air absorption, loss of vapors, and contamination. Just before sampling, rinse the bottle with the gasoline to be sampled.

3. A new hazardous materials packing system (Enclosure No. 2) employing 1-liter glass bottles and epoxy-lined 1-gallon (DOT) round cans were evaluated side-by-side for storage effects on a gasoline (Phillips J). TABLE 1 summarizes the principal properties of Phillips J gasoline, which was placed in two each 1-liter glass bottles and two each 1-gallon epoxy-lined cans, which were then stored in a laboratory safety hood for 1 month. Prior to placing gasoline in the storage vessels, they were cleaned with TAM (equal portions of toluene, acetone, and methanol), n-heptane, and nitrogen dried. The gasoline was sampled from the

TABLE 1. Characterization of Phillips J Gasoline

Lab Identification	Test Method	AL-15734-G
Induction Period, minutes	ASTM D 525	>1440
Unwashed Gum, mg/100 mL	ASTM D 381	2.2
Existent Gum, mg/100 mL	ASTM D 381	1.1
Potential Residue, 4 hours	ASTM D 873	
Unwashed Gum, mg/100 mL	ASTM D 381	3.1
Existent Gum, mg/100 mL	ASTM D 381	1.5
Aromatics, vol%	ASTM D 1319	38.4
Olefins, vol%	ASTM D 1319	15.2
Saturates, vol%	ASTM D 1319	46.4
Induction System Deposit:	Fed. Test	
100-mL volume, mg/100 mL	Method 500.1	0.1
300-mL volume, mg/300 mL		1.6

storage vessels for 0, 7, 14, 21, 28, and 31 days to determine unwashed and existent gum by D 381. This data is summarized in TABLE 2. Note that D 381 data were determined in duplicate (reported as mg/50 mL), which was then added together to give "total" mg/100 mL. The fuel in the glass bottles was protected from light using aluminum foil. The data in TABLE 2 suggest that the epoxy-lined can did not contribute to increased gum with time.

4. ASTM D 4306 (Standard Practice for Aviation Fuel Sample Containers for Tests Affected by Trace Contamination) recommends epoxy-lined containers for samples to be tested for thermal stability testing. Elsewhere, cautions are provided stating that the suitability of a batch of epoxy-lined cans should be checked prior to their use, suggesting that the curing process can vary from batch to batch. Sampling procedures for JP-4 request equilibration with the JP-4 for 24 hours prior to filling and shipping.

TABLE 2. Gum Data for Can and Bottle Gasoline Storage

	Epoxy-Lined Can No. 1	Epoxy-Lined Can No. 2	Glass Bottle No. 1	Glass Bottle No. 2
Day 0				
Unwashed Gum, D 381, mg/50 mL	0.5, 0.4	0.8, 0.8	1.0, 0.8	0.5, 0.5
Total, mg/100 mL	0.9	1.6	1.8	1.0
Existent Gum, D 381, mg/50 mL	0.5, 0.4	0.7, 0.7	1.0, 0.7	0.6, 0.3
Total, mg/100 mL	0.9	1.4	1.7	0.9
Day 7				
Unwashed Gum, D 381, mg/50 mL	0.5, 0.5	0.5, 0.3	0.7, 0.8	0.6, 0.6
Total, mg/100 mL	1.0	0.8	1.5	1.2
Existent Gum, D 381, mg/50 mL	0.5, 0.3	0.5, 0.3	0.7, 0.7	0.6, 0.6
Total, mg/100 mL	0.8	0.8	1.4	1.2
Day 14				
Unwashed Gum, D 381, mg/50 mL	0.8, 0.9	0.8, 0.7	0.6, 0.7	0.7, 0.6
Total, mg/100 mL	1.7	1.5	1.3	1.3
Existent Gum, D 381, mg/50 mL	0.8, 0.8	0.7, 0.5	0.6, 0.7	0.7, 0.4
Total, mg/100 mL	1.6	1.2	1.3	1.1
Day 21				
Unwashed Gum, D 381, mg/50 mL	0.3, 0.2	0.4, 0.1	0.7, 0.3	0.5, 0.4
Total, mg/100 mL	0.5	0.5	1.0	0.9
Existent Gum, D 381, mg/50 mL	0.3, 0.2	0.4, 0.1	0.4, 0.3	0.1, 0.2
Total, mg/100 mL	0.5	0.5	0.7	0.3
Day 28				
Unwashed Gum, D 381, mg/50 mL	0.9, 0.8	0.9, 0.8	0.4, 0.1	0.4, 0.4
Total, mg/100 mL	1.7	1.7	0.5	0.8
Existent Gum, D 381, mg/50 mL	0.8, 0.8	0.9, 0.6	0.2, 0.0	0.4, 0.0
Total, mg/100 mL	1.6	1.5	0.2	0.4
Day 31				
Unwashed Gum, D 381, mg/50 mL	0.7, 0.7	0.7, 1.0	0.6, 0.4	0.6, 0.4
Total, mg/100 mL	1.4	1.7	1.0	1.0
Existent Gum, D 381, mg/50 mL	0.6, 0.6	0.7, 0.8	0.6, 0.4	0.6, 0.4
Total, mg/100 mL	1.2	1.5	1.0	1.0

STRBE-VF, Mr. M.E. LePera
U.S. Army Belvoir Research, Development and Engineering Center
21 December 1989
Page 5

5. We recomend that the 1-liter glass sample containers (in Enclosure No. 2) be used in evaluating the method in Enclosure No. 1. These containers should be washed with TAM, n-heptane, dried, and then rinsed with test fluid (gasoline) prior to filling (leaving a 5-percent ullage volume).

6. Please contact L.L. Stavinoha at (512) 522-2586 for discussions regarding this letter.

Very truly yours,

S.J. Lestz, Director

Leo L. Stavinoha

L.L. Stavinoha, Manager
Fuel Properties and Applications

SJL/LLS/lap
(LLS.A)

Enclosures

cf: U.S. Army Belvoir Research, Development and Engineering Center, Attn:
STRBE-VF, Messrs. T.C. Bowen and F.W. Schaekel
Belvoir Fuels and Lubricants Research Facility (SwRI), Attn: L.A. McInnis,
S.R. Westbrook, and B.K. Bailey

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SECRETARY OF THE SOCIETY

A TENTATIVE METHOD FOR OXIDATION STABILITY OF MOTOR GASOLINES (TOTAL POTENTIAL GUM METHOD)

(A Modification of ASTM D 873-IP 138)

1. SCOPE

1.1 This method covers the determination of the tendency of motor gasoline (**Danger**—See Annex A1.4) to form gum deposits under accelerated aging conditions in predicting storage stability.

Caution: The method[1] is not intended for the determination of the stability of gasoline components particularly those with a high percentage of low boiling unsaturated compounds as they may cause explosive conditions within the apparatus.

1.2 This standard may involve hazardous materials, operations, and equipment. This standard does not purport to address all of the safety problems associated with its use. It is the responsibility of whoever uses this standard to consult and establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

NOTE 1—The accepted unit of pressure is the pascal (Pa) for ASTM methods. The conventional pound per square inch (psi) value is included parenthetically. The Institute of Petroleum uses the bar as a pressure measurement. Conversion of units may be obtained as follows:

To convert from pound-force/inch^2 (psi) to pascal (Pa) multiply by 6.894757 × 10^3.
To convert from pound-force/inch^2 (psi) to bar multiply by 0.06894757.
To convert from bar to pascal (Pa) multiply by 10^5.

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[1] Further information can be found in the June 1978, January 1979, and June 1986 editions of the *Institute of Petroleum Review.*

2. APPLICABLE DOCUMENTS

2.1 ASTM Standards:

D 381 Test Method for Existent Gum in Fuels by Jet Evaporation (Air Jet Procedure)[2]
D 525 Test Method for Oxidation Stability of Gasoline (Induction Period Method)[2]
D 4057 Practice for Manual Sampling of Petroleum and Petroleum Products[3]
E 1 Specification of ASTM Thermometers[4]

3. SUMMARY OF METHOD

3.1 The fuel is oxidized for 6 hours under prescribed conditions in a bomb filled with oxygen (**Danger**--See Annex A1.6). The amounts of deterioration products collected from the aged fuel and the toluene-acetone (gum solvent) soluble portion of the deposit on the glass sample container are weighed altogether and reported as total unwashed gum. The heptane insoluble residue from the unwashed gum is weighed and reported as total (washed) existent gum.

4. SIGNIFICANCE

4.1 The results (of these tests) may be used to indicate storage stability of gasolines that have low initial D 381 existent gum values. The tendency of fuels to form gum in this test has not been correlated with (and may vary markedly from) the formation of gum under actual field storage conditions.

5. DESCRIPTION OF TERMS SPECIFIC TO THIS STANDARD

5.1 Total Unwashed Gum—deterioration products present at the end of a specific aging period. These deterioration products are collected from the aged fuel and from the toluene-acetone soluble portion of the deposit on the glass sample container. Total gum is obtained as a nonvolatile residue by evaporating together the aged fuel and the toluene-acetone washings from the glass sample container using a preheated stream of air.

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[2] Annual Book of ASTM Standards, Vol 05.01.

[3] Annual Book of ASTM Standards, Vol 05.03.

[4] Annual Book of ASTM Standards, Vols 05.03 and 14.01.

5.2 Existent Gum—The evaporation residue of the heptane-insoluble portion of the total unwashed gum.

6. APPARATUS

6.1 Oxidation Bomb, Glass Sample Container and Cover, Accessories and Pressure Gage, as described in the Appendix to ASTM Method D 525-IP 40.

6.2 Thermometer, having a range as shown below and conforming to the requirements as prescribed in Specification E 1, or specification for IP thermometers:

	Thermometer Number	
Thermometer Range	ASTM	IP
204° to 218°F	22F	24F
95° to 103°C	22C	24C

6.3 Drying Oven—Air oven maintained at 100° to 150°C (212° to 302°F).

6.4 Tongs, corrosion-resistant, steel.

6.5 Oxidation Bath, as described in the Appendix to ASTM Method D 525-IP 40. The liquid (**Caution**—Use protective clothing and tongs) shall be water or a mixture of ethylene glycol and water, as required. The temperature may be controlled thermostatically at 100° ± 0.1°C (212° ± 0.2°F), or by maintaining it at its boiling point, which must be between 99.5° and 100.5°C (211° and 213°F).

6.6 Air jet heater block for performing ASTM Method D 381-IP 131.

7. MATERIAL

7.1 Gum Solvent (**Danger**—See Annex A1.1)—A mixture of equal volumes of toluene (**Danger**—See Annex A1.2) and acetone (**Danger**—See Annex A1.7).

7.2 Oxygen (**Warning**—See Annex A1.6)—Commercially Available Extra Dry Oxygen, of not less than 99.6% purity can be used without further purification.

8. SAMPLING

8.1 Sample in accordance with the procedure for oxidation stability as described in Section 11.4 of Standard D 4057 and in the appropriate sections of Part IV of IP Standards for Petroleum and Its Products.

9. PREPARATION OF APPARATUS

9.1 Thoroughly clean a glass sample container to remove traces of any adhering material. Immerse the container and its cover in detergent cleaning solution (**Caution**—See Annex A1.5). The type of detergent and conditions for its use need to be established in each laboratory. The criterion for satisfactory cleaning shall be a matching of the quality of that obtained with chromic acid cleaning solution (**Danger**—See Annex A1.3) on used sample containers and covers (fresh chromic acid, 6-hour soaking period, rinsing with distilled water and drying). For this comparison visual appearance and weight loss on heating the glassware under test conditions may be used. Detergent cleaning avoids the potential hazards and inconveniences related to handling corrosive chromic acid solutions. The latter remains as the reference cleaning practice and as such may function as an alternative to the preferred procedure—cleaning with detergent solutions.

9.2 Remove glassware from the cleaning solution by means of corrosion- resistant steel tongs and handle only with tongs thereafter. Wash thoroughly, first with tap water, then with distilled water, and dry in an oven at 100° to 150°C (212° to 302°F) for at least 1 hour. Cool the sample containers and cover for at least 2 hours in the cooling vessel.

9.3 Drain any gasoline from the bomb and wipe the inside of the bomb and lid, first with a clean cloth moistened with gum solvent and then with a clean dry cloth. Remove the filler rod from the stem and carefully clean any gum or gasoline from stem, rod, and needle valve with gum solvent. The bomb and all connecting lines shall be thoroughly dry before each test is started.

Caution: Ensure all components of the equipment are thoroughly cleaned before storage and reuse because volatile peroxides may be formed during a test.

9.4 If a thermostatically controlled constant temperature oxidation bath is used, adjust the temperature to 100° ± 0.1°C (212° ± 0.2°F) and maintain it within this temperature range for the duration of the test.

9.5 If a boiling water oxidation bath is used, adjust the temperature within the range of 99.5° to 100.5°C (211° to 213°F) by the addition of water or a higher boiling liquid such as ethylene glycol.

10. PROCEDURE

10.1 Allow the empty bomb, the glass sample container, and the gasoline (**Danger**—See Annex A1.4) to be tested to attain equilibrium at a temperature of 15° to 25°C (59° to 77°F). Place the glass sample container in the bomb and add 100 ± 1 mL of sample. Cover the sample container, close the bomb, and using the quick release air-coupling, introduce oxygen (**Danger**—See Annex A1.6) until a pressure of 689 to 703 kPa (100 to 102 psi) is attained. Slowly exhaust the bomb through the needle valve at a rate not to exceed 345 kPa/min (50 psi/min). Repeat the charging and exhausting once more in order to flush out the air originally present. Introduce oxygen again until a pressure of 689 to 703 kPa (100 to 102 psi) is attained and observe for leaks, ignoring an initial rapid drop in pressure [generally not over 41.4 kPa (6 psi)] which may be observed because of the solution of oxygen in the sample. When leaks are eliminated as indicated by a pressure drop less than 13.8 kPa (2 psi) in 10 minutes, proceed with the test.

10.2 Place the charged bomb in one of the described oxidation baths, being careful to avoid spilling gasoline from the sample container, and record the time of immersion as the starting time. Leave the bomb in the oxidation bath for the specified 6-hour aging time or the equivalent time based on TABLE 1. If a boiling water bath (**Caution**—Hot liquid. Use protective clothing and tongs) is used, and should the temperature at the start of a test vary from 100°C (212°F) by more than ± 0.1°C (0.2°F), adjust the aging time by the correction factors given in Table 1. If a break point occurs before completion of the specified 6-hour aging time, discontinue the test. The "break point" is that point preceded by a pressure drop of exactly 13.8 kPa (2 psi) in 15 minutes and succeeded by a drop of not less than 13.8 kPa (2 psi) in 15 minutes.

10.3 At the completion of the specified 6-hour aging time, remove the bomb from the bath and cool rapidly with water while the charging valve is still closed. Release the pressure slowly through the needle valve at a rate not to exceed 345 kPa/min (50 psi/min). Take the bomb apart and remove the sample container.

10.4 Transfer the contents of the sample container to a flask. Wash the interior of the glass sample container twice, mixing thoroughly with 10-mL portions of gum solvent (**Danger**—See Annex

A1.1) to remove any gum. Add these mixtures to the oxidized gasoline in the flask for the determination of total gum. If a precipitate remains adhered to the sample container after two washings, so note.

10.5 Divide the liquid obtained in 10.4 into two equal portions (within 2 mL), and determine the unwashed gum therein by the procedure and test conditions described in ASTM Method D 381-IP 131 (air jet), using in each test the entire half portion instead of the 50-mL sample specified in ASTM Method D 381-IP 131. Record the sum of the increase in weight of the two gum beakers as total unwashed gum.

10.6 Using the two gum beakers from 10.5, determine the existent (washed) gum therein by the procedure and test conditions described for existent gum in ASTM Method D 381-IP 131. Record the sum of the increase in weight of the two gum beakers as total existent gum.

11. REPORT

11.1 Report "6-hour" total unwashed gum in mg/100 mL.

11.2 Report "6-hour" total (washed) existent gum in mg/100 mL.

12. PRECISION

12.1 The precision of this method has not been determined.

TABLE 1. AGING TIME CORRECTION FACTORS

{Note— To obtain the equivalent aging time at the operating temperature, multiply the specified 6-hour aging time for 100°C (212°F) by the correction factor.}

Temperature,		Correction Factor
°F	°C	
211.0	99.5	1.06
211.2	99.6	1.04
211.4	99.7	1.03
211.6	99.8	1.02
212.0	100.0	1.00
212.4	100.2	0.98
212.6	100.3	0.97
212.8	100.4	0.96
213.0	100.5	0.95

ANNEX

A1. PRECAUTIONARY STATEMENTS
MANDATORY INFORMATION

A1.1 GUM SOLVENT

DANGER—Extremely flammable. Vapors harmful. Vapors may cause fire.
Keep away from heat, sparks, and open flame.
Keep container closed.
Use with adequate ventilation.
Vapors may spread long distances and ignite explosively.
Avoid build-up of vapors and eliminate all sources of ignition, especially nonexplosion-proof electrical apparatus and heaters.
Avoid prolonged breathing of vapor or spray mist.
Avoid contact with eyes and skin.

A1.2 TOLUENE

WARNING—Flammable. Vapor harmful. Keep away from heat, sparks, and open flame. Keep container closed. Use with adequate ventilation. Avoid breathing of vapor or spray mist. Avoid prolonged or repeated contact with skin.

A1.3 CHROMIC ACID (CLEANING SOLUTION)

DANGER—Causes severe burns. A recognized carcinogen. Strong oxidizer- contact with organic material may cause fire. Hygroscopic.
Do not get in eyes, on skin, on clothing.
Avoid breathing vapor or mist.
Keep container closed.
Use with adequate ventilation.
Do not take internally.
Wash thoroughly after handling.
Use protective clothing and goggles when handling.

A1.4 GASOLINE (INCLUDING LEADED GASOLINE)

DANGER—Extremely flammable. Vapors harmful if inhaled. Vapors may cause flash fire. May contain toxic lead antiknock compounds. Harmful if absorbed through skin.
Keep away from heat, sparks, and open flame.
Keep container closed.
Use with adequate ventilation.
Avoid build-up of vapors and eliminate all sources of ignition, especially nonexplosion-proof electrical apparatus and heaters.
Avoid prolonged breathing of vapor or spray mist.
Avoid prolonged or repeated skin contact.

A1.5 DETERGENT

CAUTION—Harmful if taken internally. Continued use may cause skin drying and chapping. Use rubber gloves and skin cream as needed.

A1.6 OXYGEN

WARNING—Oxygen vigorously accelerates combustion.
Keep oil and grease away. Do not use oil or grease on regulators, gages, or control equipment.
Use only with equipment conditioned for oxygen service by carefully cleaning to remove oil, grease, and other combustibles.
Keep combustibles away from oxygen and eliminate ignition sources.
Keep surfaces clean to prevent ignition or explosion, or both, on contact with oxygen.
Always use a pressure regulator. Release regulator tension before opening cylinder valve.
All equipment and containers used must be suitable and recommended for oxygen service.
Never attempt to transfer oxygen from cylinder in which it is received to any other cylinder.
Do not mix gases in cylinders.
Do not drop cylinder. Make sure cylinder is secured at all times.
Keep cylinder valve closed when not in use.
Stand away from outlet when opening cylinder valve.
Keep cylinder out of sun and away from heat.
Keep cylinder from corrosive environment.
Do not use cylinder without label.
Do not use dented or damaged cylinders.
For technical use only. Do not use for inhalation purposes.
Use only in well-ventilated area.
See compressed gas association booklets G-4 and G4.1 for details of safe practice in the use of oxygen.

A1.7 ACETONE

DANGER—Extremely flammable. Vapors may cause flash fire.
Keep away from heat, sparks, and open flame.
Keep container closed.
Use with adequate ventilation.
Avoid build-up of vapors.
Eliminate all sources of ignition and especially nonexplosion-proof electrical apparatus and heaters.
Avoid prolonged breathing of vapor or spray mist.
Avoid contact with eyes or skin.

SturdeeSeal PACKAGING SYSTEM

NEW! HAZARDOUS MATERIALS PACKAGING SYSTEM

Complies with D.O.T. and UPS...
Conforms with U.N. Requirements...
and no warning label is required in most cases.*

*The SturdeeSeal™ system is so effective that the D.O.T. has exempted it from having to bear an outside warning label when shipping most hazardous materials.** The United Nations Specification 4G/ x 15/S/86. D.O.T. Specifications 12B30 and 12A20, and D.O.T. Exemption #DOT-E-9166 are printed on the outside of the shipper to facilitate UPS and international shipments.

The basic component of the SturdeeSeal™ System is the PVC-coated glass bottle which is available in 1 litre (approx. 32 oz.), 500cc or 950cc sizes. The PVC coating is a clear, high-tensile plastisol skin which is fitted snugly over the bottle and helps to contain contents if the inner glass bottle is broken. A thick blanket and two pads of absorbent vermiculite are provided to envelop the bottle and cushion it within the 25-lb. tinplate steel canister. After the canister lid is secured with tape, the canister is placed into the 4-mil low density polyethylene bag. The bagged canister is then placed into the corrugated insert of the 275# double wall shipping carton. Nonasphaltic, water-activated carton tape (included) is used to seal the carton.

****The major exception is PCBs (polychlorinated biphenyls). These may be shipped in SturdeeSeal™ via UPS, but must bear a special warning label.***

New SturdeeSeal™ Packaging System features vermiculite blanket and pads to provide optimum protection in the unlikely event that breakage should occur.

SturdeeSeal™ Packaging System comes preassembled, and includes the necessary components to ship hazardous materials via UPS or overseas. Here's how it works:

1. Fill bottle to shoulder. Replace cap; secure tape around cap and neck of bottle.
2. Wrap bottle in the vermiculite blanket, add pads and place bottle in the steel canister.
3. Place lid on the canister and secure lid with strips of polypropylene tape.
4. Put canister into the polypropylene bag, twist the end and tie bag within itself.
5. Place bagged canister into corrugated insert, push corners in to secure can.
6. Seal box with 3" tape. Put shipping name and identification number on box.

Each SturdeeSeal™ Shipper includes:

- PVC plasticoated glass bottle (in choice of 3 sizes) with Teflon-lined cap
- Full friction .25-lb. tinplate steel canister with welded sideseam
- One vermiculite blanket wrap
- Two vermiculite cushioning pads
- Polypropylene tape to wrap around cap and across canister lid
- 275# double wall shipping carton with preprinted instructions, D.O.T. Specification and Exemption Numbers, and U.N. Standard Marking
- 3" nonasphaltic, water-activated carton tape for sealing shipping carton
- One copy of DOT-E-9168 (Exemption Paper)
- Assembly instructions

SAVE 50% to 75%
by shipping hazardous materials
via UPS with SturdeeSeal™

This new D.O.T. approved packaging system allows safe shipments via UPS at a savings of up to 75% compared with shipping similar products via common carriers.

For Priority Service
USE YOUR
ACCOUNT
NUMBER

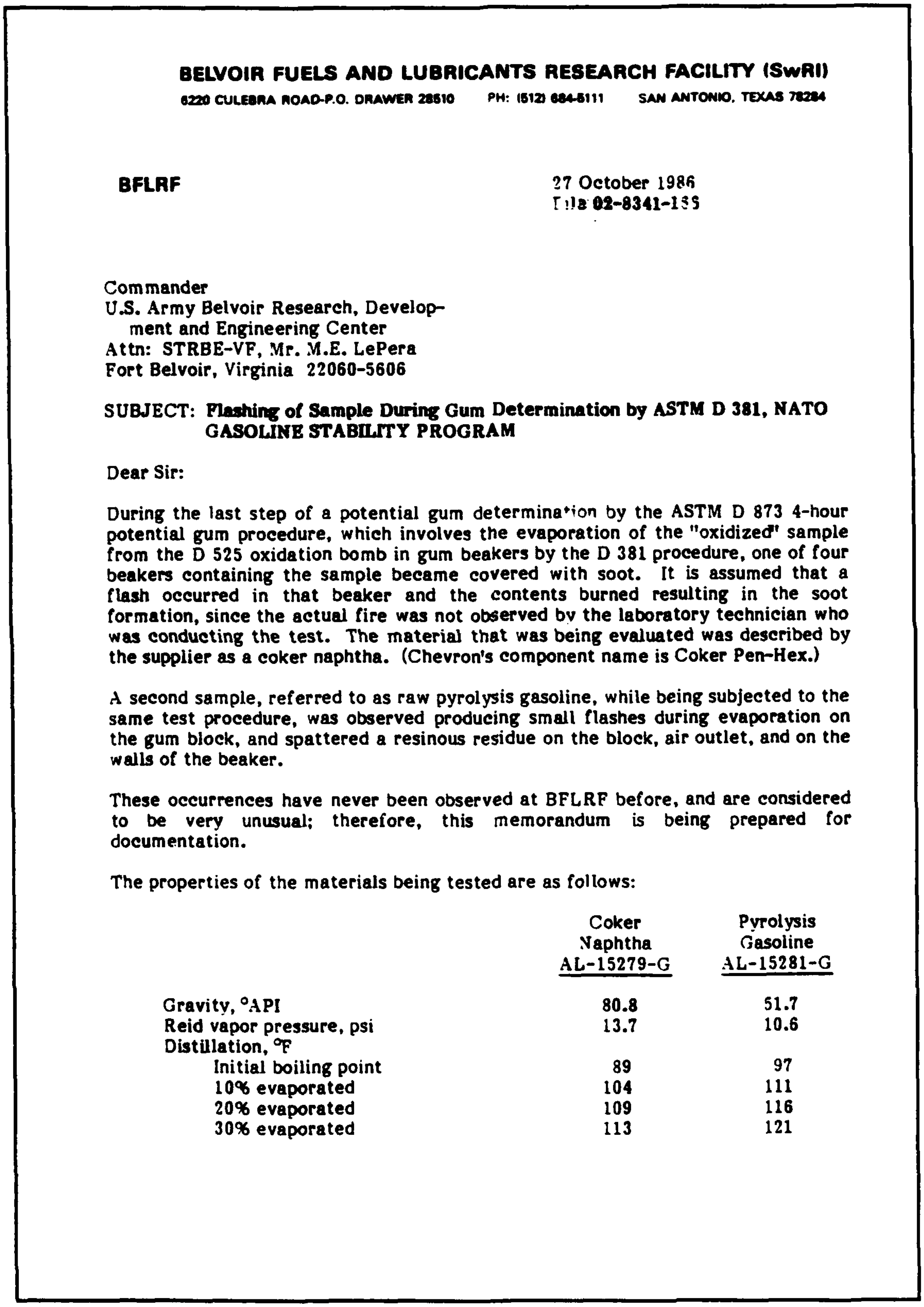
PRICES *shown are per each SturdeeSeal™ Shipper*

STYLE	BOTTLE CAPACITY	BOTTLE OPENING	1-11	12-23	24-95	96-191	192+
HMS-33	1 litre	33mm	20.00	18.20	16.70	15.40	14.75
HMS-950	950cc	53mm	23.00	20.00	19.75	17.50	16.50
HMS-500	500cc	53mm	21.50	19.85	17.50	16.50	15.50

Enclosure No. 2

APPENDIX C

Flashing of Sample During Gum Determination by ASTM D 381, NATO Gasoline Stability Program



BELVOIR FUELS AND LUBRICANTS RESEARCH FACILITY (SwRI)
6220 CULEBRA ROAD-P.O. DRAWER 28510 PH: (512) 684-5111 SAN ANTONIO, TEXAS 78284

BFLRF

27 October 1986
File 02-8341-135

Commander
U.S. Army Belvoir Research, Development and Engineering Center
Attn: STRBE-VF, Mr. M.E. LePera
Fort Belvoir, Virginia 22060-5606

SUBJECT: **Flashing of Sample During Gum Determination by ASTM D 381, NATO GASOLINE STABILITY PROGRAM**

Dear Sir:

During the last step of a potential gum determination by the ASTM D 873 4-hour potential gum procedure, which involves the evaporation of the "oxidized" sample from the D 525 oxidation bomb in gum beakers by the D 381 procedure, one of four beakers containing the sample became covered with soot. It is assumed that a flash occurred in that beaker and the contents burned resulting in the soot formation, since the actual fire was not observed by the laboratory technician who was conducting the test. The material that was being evaluated was described by the supplier as a coker naphtha. (Chevron's component name is Coker Pen-Hex.)

A second sample, referred to as raw pyrolysis gasoline, while being subjected to the same test procedure, was observed producing small flashes during evaporation on the gum block, and spattered a resinous residue on the block, air outlet, and on the walls of the beaker.

These occurrences have never been observed at BFLRF before, and are considered to be very unusual; therefore, this memorandum is being prepared for documentation.

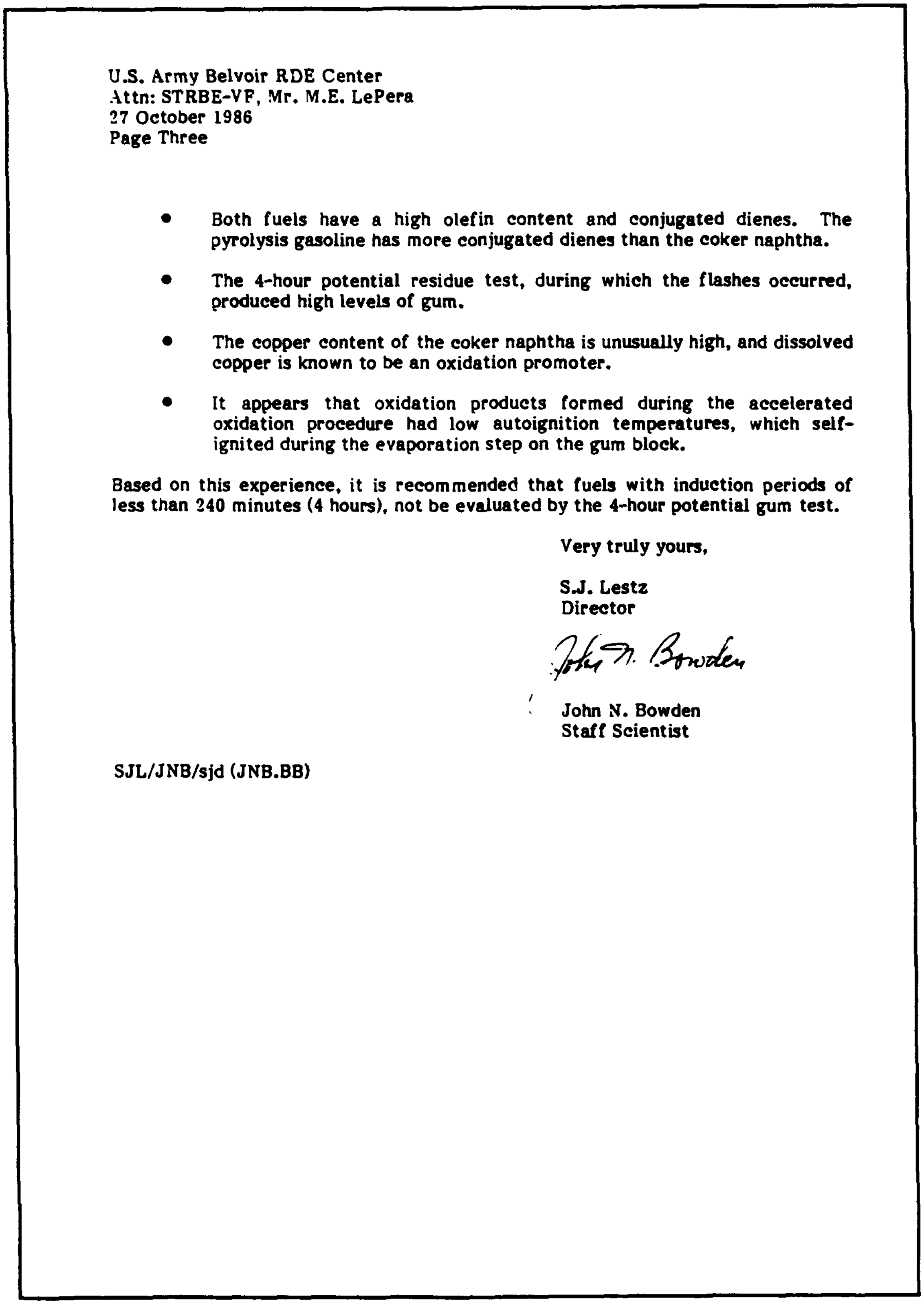
The properties of the materials being tested are as follows:

	Coker Naphtha AL-15279-G	Pyrolysis Gasoline AL-15281-G
Gravity, °API	80.8	51.7
Reid vapor pressure, psi	13.7	10.6
Distillation, °F		
Initial boiling point	89	97
10% evaporated	104	111
20% evaporated	109	116
30% evaporated	113	121

	Coker Naphtha AL-15279-G	Pyrolysis Gasoline AL-15281-G
40% evaporated	117	127
50% evaporated	122	136
60% evaporated	128	147
70% evaporated	135	166
80% evaporated	146	201
90% evaporated	162	315
95% evaporated	175	355
End point	202	370
Residue, vol%	1	1
Loss, vol%	1	1
Induction period, minutes (D 525)	105	105
4-hour potential residue (modified D 873)	48.7	775
Unwashed gum, mg/100 mL	13.8	22.8
Existent gum, mg/100 mL (heptane washed)	0.6	5.1
FIA		
Saturates, vol%	52.1	17.0
Olefins, vol%	46.3	40.7
Aromatics, vol%	1.6	42.3
Copper, ppb (ICP)	548	27
Research octane number	85.5	97.4
Motor octane number	74.2	79.68
ISD rating, mg/100 mL	0	4.1
Peroxide number	0.15	0.20
Color, D 1500	<0.5	1.0
Color, D 156	+10	<-16
Copper corrosion, rating	1A	1A
Conjugated dienes, wt%	2.8	8.3

Several properties of these materials may have contributed to the flash fires that apparently occurred.

- The coker naphtha is a narrow, low boiling fraction with a high vapor pressure.
- The pyrolysis gasoline has a broader boiling range and an intermediate vapor pressure.
- Both have short induction periods.



U.S. Army Belvoir RDE Center
Attn: STRBE-VF, Mr. M.E. LePera
27 October 1986
Page Three

- Both fuels have a high olefin content and conjugated dienes. The pyrolysis gasoline has more conjugated dienes than the coker naphtha.
- The 4-hour potential residue test, during which the flashes occurred, produced high levels of gum.
- The copper content of the coker naphtha is unusually high, and dissolved copper is known to be an oxidation promoter.
- It appears that oxidation products formed during the accelerated oxidation procedure had low autoignition temperatures, which self-ignited during the evaporation step on the gum block.

Based on this experience, it is recommended that fuels with induction periods of less than 240 minutes (4 hours), not be evaluated by the 4-hour potential gum test.

Very truly yours,

S.J. Lestz
Director

John N. Bowden

John N. Bowden
Staff Scientist

SJL/JNB/sjd (JNB.BB)

APPENDIX D

Change in Composition of Reference Gasoline; MIL-G-53042

BELVOIR FUELS AND LUBRICANTS RESEARCH FACILITY (SwRI)
6220 CULEBRA ROAD-P.O. DRAWER 28510 PH: (512) 684-5111 SAN ANTONIO, TEXAS 78284

BFLRF

File: 02-8341-166
6 January 1987

Commander
U.S. Army Belvoir Research, Development and Engineering Center
Attn: STRBE-VF, Mr. M.E. LePera
Fort Belvoir, Virginia 22060-5606

Subject: **Change in Composition of Reference Gasoline; MIL-G-53042**

References:
1) Letter from STRBE-VF (Mr. LePera) to Belvoir Fuels and Lubricants Research Facility (Mr. Lestz), dated 28 February 1986
2) Letter from Belvoir Fuels and Lubricants Research Facility (Mr. Lestz) to STRBE-VF (Mr. LePera) entitled, "Reply to Questions on Proposed Revisions to MIL-G-53042," dated 31 March 1986

Dear Sir:

Reference 1 raises questions regarding certain proposed changes to MIL-G-53042; specifically whether the reference gasoline in the specification is too stable, and if so, how to make it less stable.

Reference 2 presents a consensus opinion that a change in the composition of the reference gasoline is desirable because it is too stable. A short, empirically oriented program was planned to determine the effect of several compounds on the induction period of reference gasoline. Results are reported here.

The ASTM D 525 induction period of unaltered reference fuel has been shown to be in excess of 960 minutes (a point at which the test is normally ended when no break point is observed).

The short research program showed that addition of 0.2 vol% of (any one of) several diolefinic compounds to the reference gasoline produced a clear break point. Induction period varied from 465-1005 minutes. As shown in Figure 1, the induction period is a function of diolefin concentration. At equal concentrations of 0.2 percent, the diolefins of highest molecular weight produce the lowest induction periods.

Hexadienes, in particular, are effective and readily available. Because the supplier indicated that all diolefins which are available contain 0.01 percent by weight of the preservative BHT, an evaluation was made for two differing lots of 2,5-dimethyl-2,4-hexadiene. The following effect was observed:

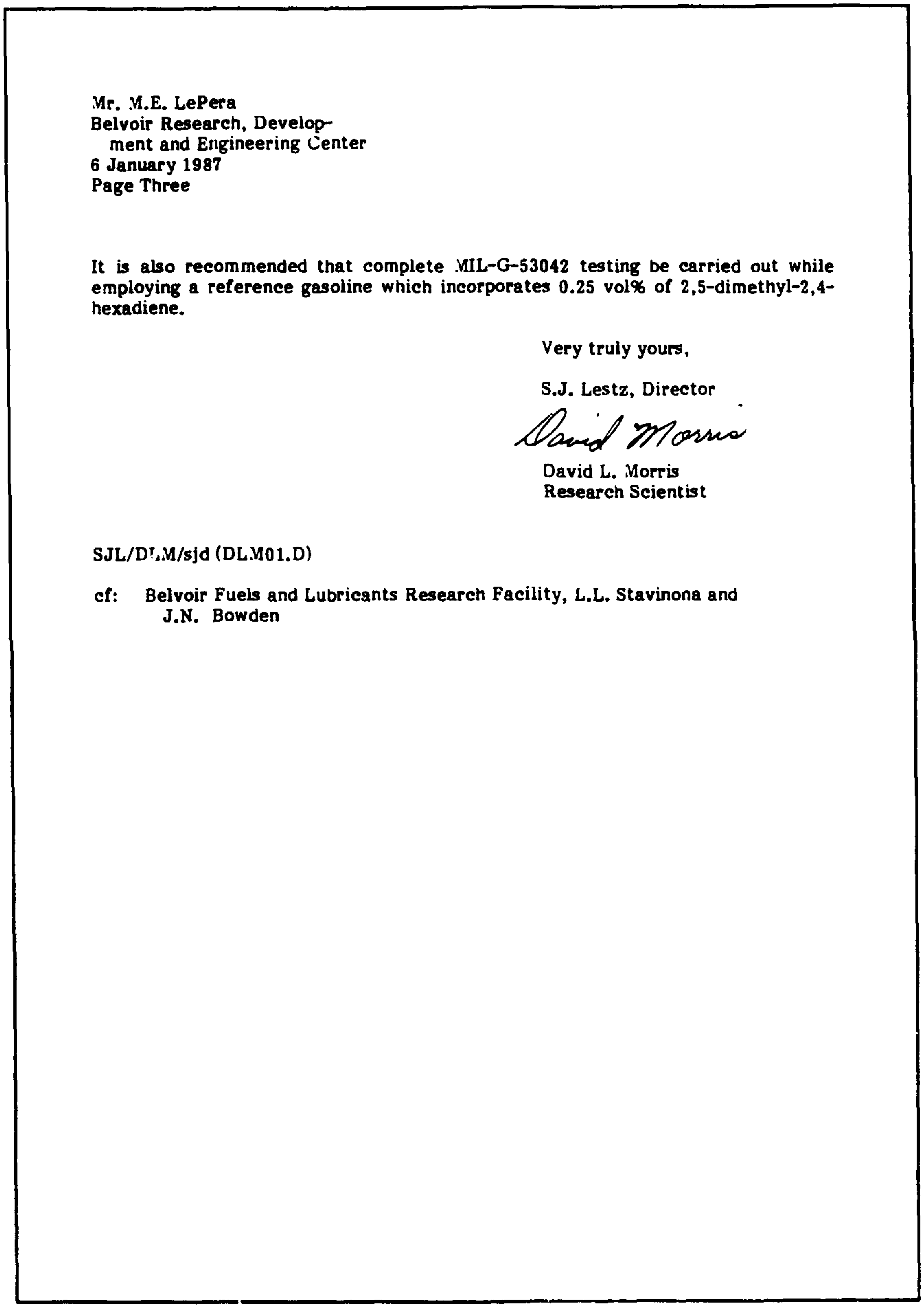
Hexadiene Concentration, vol%	D 525 Induction Period, minutes	
	Lot "1"	Lot "2"
0.2	555	465
0.5	150	120

These results indicate good agreement considering that four distinct blends are involved, and that repeatability for ASTM D 525 is 5 percent at a 95 percent confidence level.

In order to evaluate the effect of diolefin conjugation on induction period, samples were made using non-conjugated 2,5-dimethyl-1,5-hexadiene and the conjugated counterpart, 2,5-dimethyl-2,4-hexadiene, each at 0.1 vol% concentration in unaltered reference fuel. The conjugated diene generated an 855-minute induction period, compared to >960 minutes for the non-conjugated isomer (the unaltered fuel alone also tested >960 minutes). This effect conforms to the expected relative reactivity based on chemistry. It is interesting to note, however, that mixtures of this conjugated diolefin in pure isooctane (at concentrations of 0.2 and 0.5 percent) generated induction periods >960 minutes. It is concluded, therefore, that the D 525 induction period test is influenced by a synergism between conjugated diolefins and the original components of reference gasoline, rather than being influenced by the presence of conjugated diolefins solely as a concentration effect.

Mixtures containing 0.2-0.5% 2,5-dimethyl-2,4-hexadiene in unaltered reference gasoline were treated with AO-31 antioxidant (hindered phenol). Treated material was evaluated by D 525 both in the presence and absence of Copper II cyclohexanebutyrate. Results shown in Figure 2 indicate that a blend containing 0.2-0.5 percent of the hexadiene can be used to determine antioxidant effects in accordance with the procedures of MIL-G-53042.

It is recommended that MIL-G-53042 be revised to incorporate 0.25 vol% of 2,5-dimethyl-2,4-hexadiene. This should produce a reference gasoline possessing an induction period in the range of 360-480 minutes.



Mr. M.E. LePera
Belvoir Research, Development and Engineering Center
6 January 1987
Page Three

It is also recommended that complete MIL-G-53042 testing be carried out while employing a reference gasoline which incorporates 0.25 vol% of 2,5-dimethyl-2,4-hexadiene.

Very truly yours,

S.J. Lestz, Director

David Morris

David L. Morris
Research Scientist

SJL/DLM/sjd (DLM01.D)

cf: Belvoir Fuels and Lubricants Research Facility, L.L. Stavinona and J.N. Bowden

Figure 1: Effect of Diolefin on MIL-G-53042 Reference Gasoline

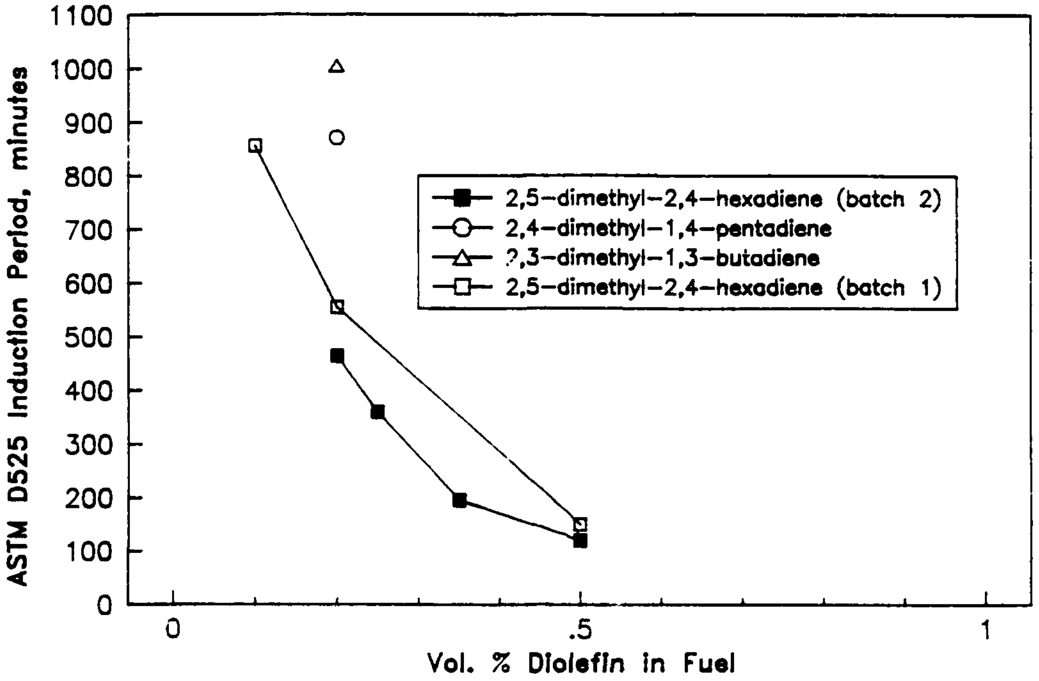
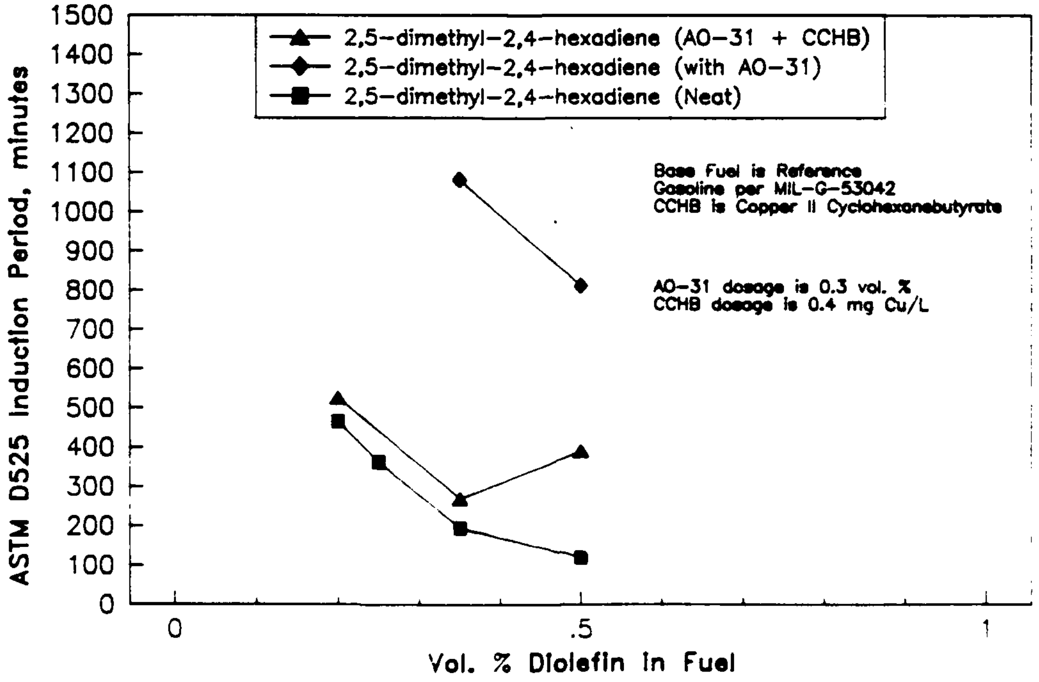


Figure 2: Effect of Diolefin, Antioxidant, and Copper Salt



Base Fuel is Reference
Gasoline per MIL-G-53042
CCHB is Copper II Cyclohexanebutyrate

AO-31 dosage is 0.3 vol. %
CCHB dosage is 0.4 mg Cu/L

APPENDIX E

Data Summary Figures

APPENDIX E

Data Summary Figures

In this appendix, data for Phases I through IV are illustrated in Figures E-1 through E-4. Each phase illustrates weeks in ambient storage, weeks in 43°C storage, and weeks in 54°C storage versus unwashed gums, existent gums, peroxide number, and ISD rating. Thus each phase has 12 graphs.

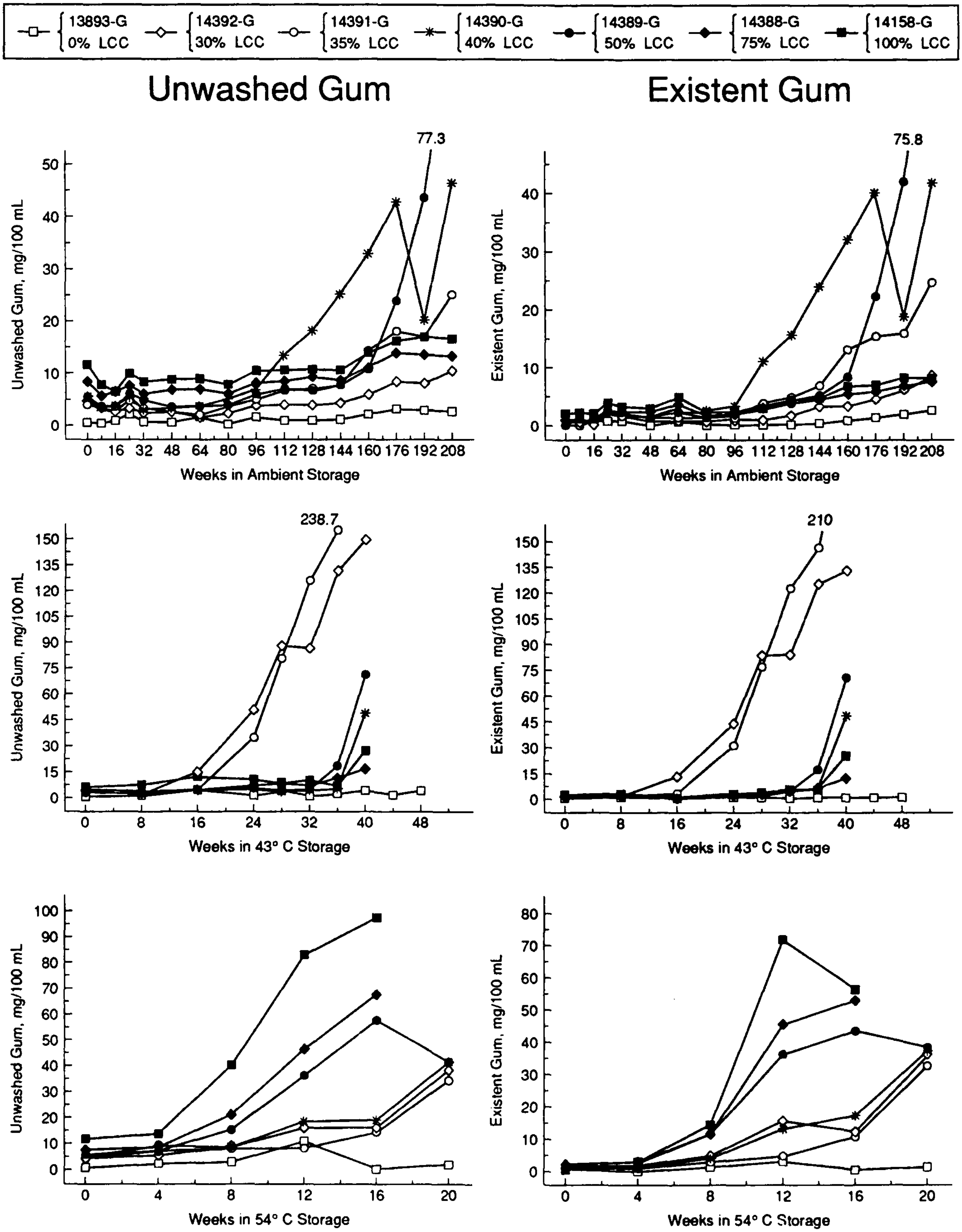
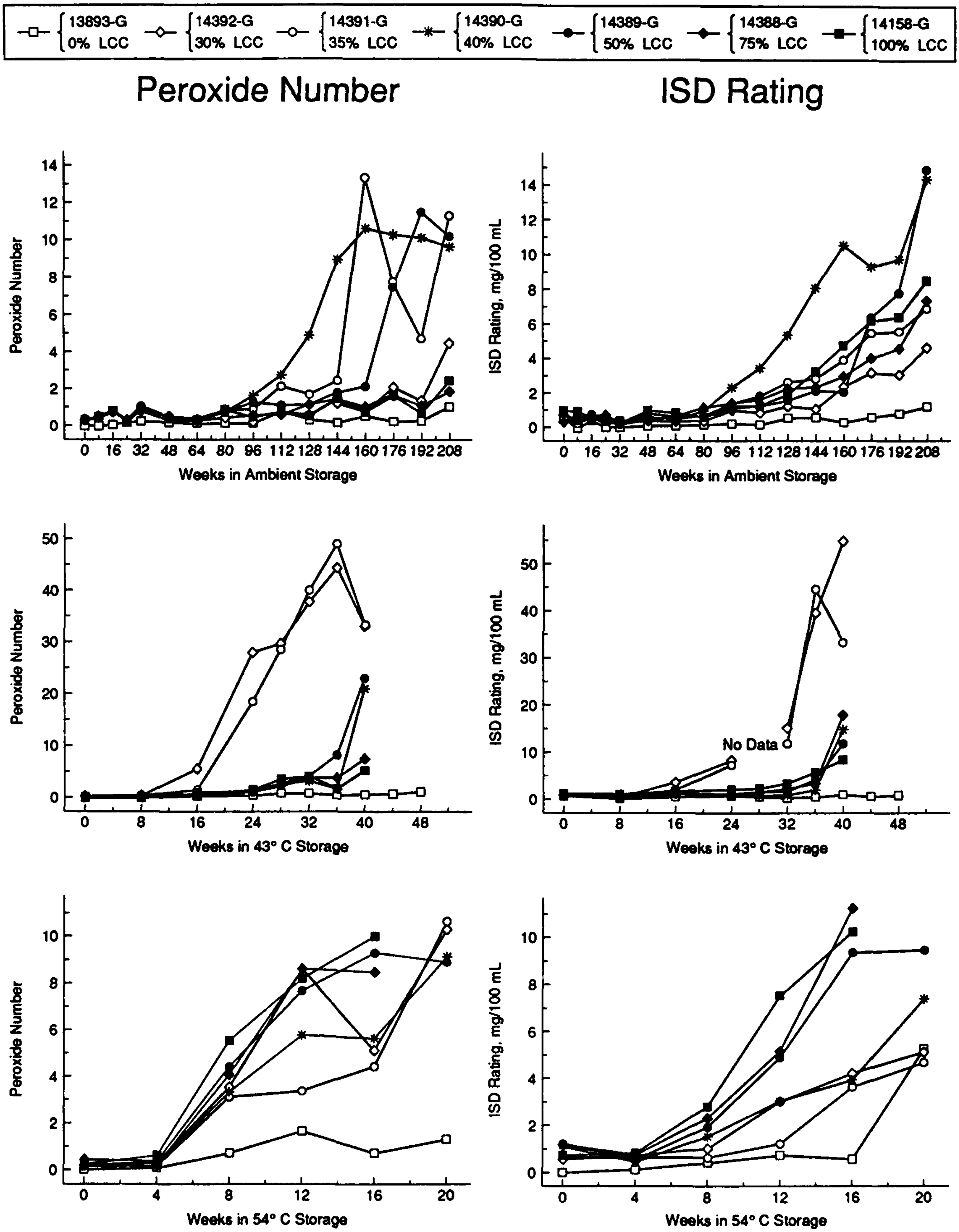


Figure E-1. Phase I data



13893-G 0% LCC
14392-G 30% LCC
14391-G 35% LCC
14390-G 40% LCC
14389-G 50% LCC
14388-G 75% LCC
14158-G 100% LCC
Peroxide Number
ISD Rating
Peroxide Number
0
2
4
6
8
10
12
14
0 16 32 48 64 80 96 112 128 144 160 176 192 208
Weeks in Ambient Storage
ISD Rating, mg/100 mL
0
2
4
6
8
10
12
14
0 16 32 48 64 80 96 112 128 144 160 176 192 208
Weeks in Ambient Storage
Peroxide Number
0
10
20
30
40
50
0 8 16 24 32 40 48
Weeks in 43° C Storage
ISD Rating, mg/100 mL
0
10
20
30
40
50
No Data
0 8 16 24 32 40 48
Weeks in 43° C Storage
Peroxide Number
0
2
4
6
8
10
0 4 8 12 16 20
Weeks in 54° C Storage
ISD Rating, mg/100 mL
0
2
4
6
8
10
0 4 8 12 16 20
Weeks in 54° C Storage

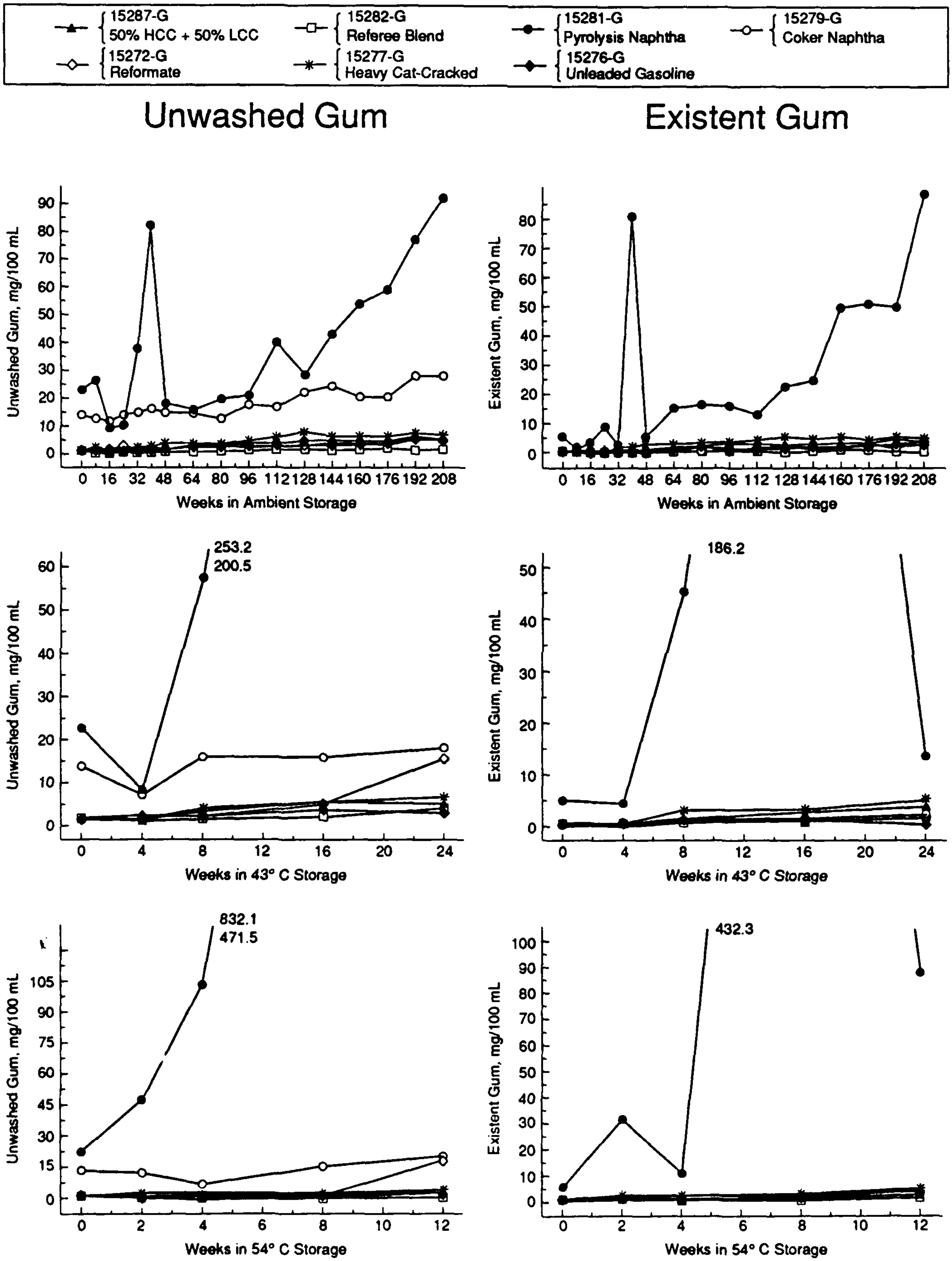
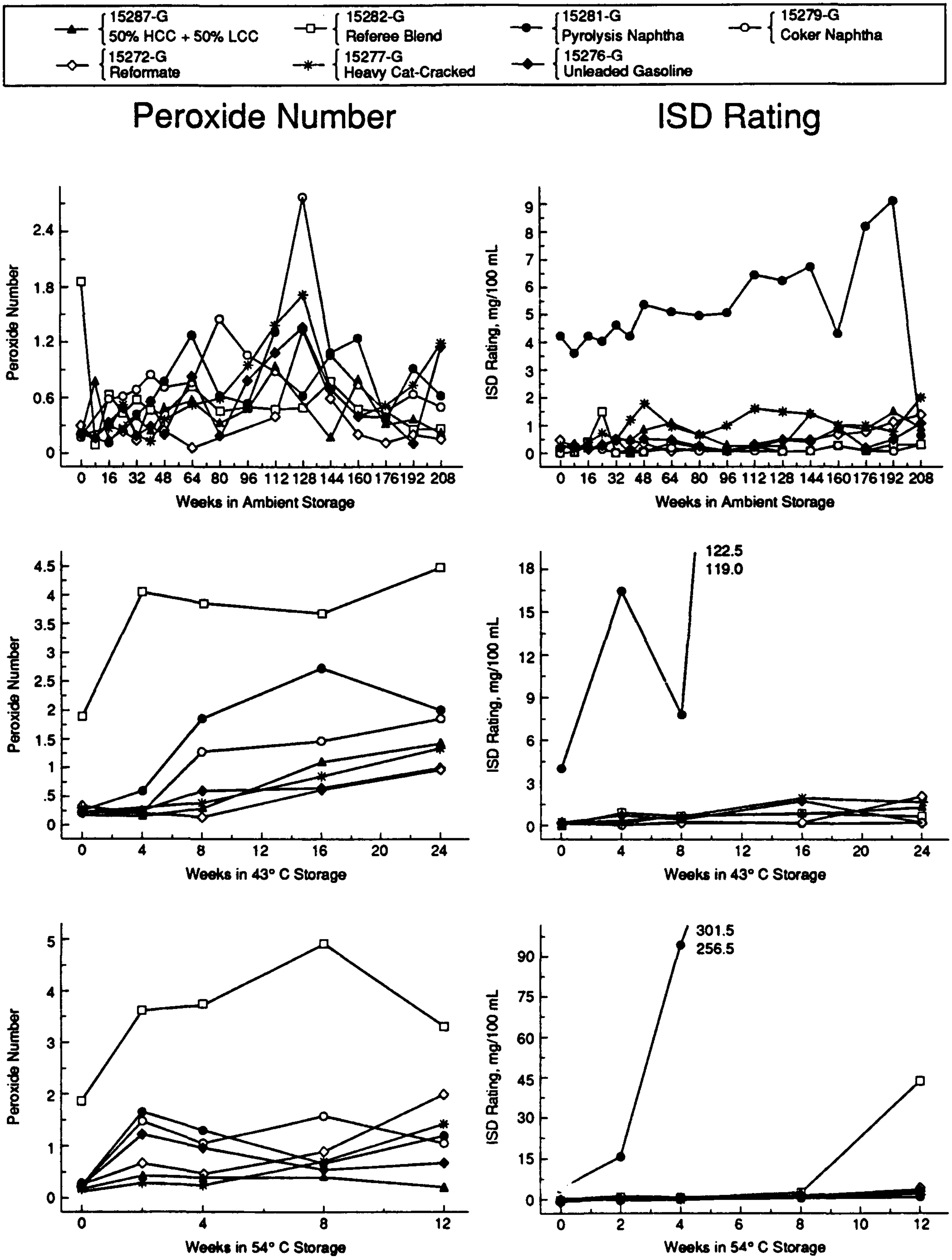


Figure E-2. Phase II data


15287-G 50% HCC + 50% LCC
15282-G Referee Blend
15281-G Pyrolysis Naphtha
15279-G Coker Naphtha
15272-G Reformate
15277-G Heavy Cat-Cracked
15276-G Unleaded Gasoline
Peroxide Number
ISD Rating
Peroxide Number
0
0.6
1.2
1.8
2.4
0 16 32 48 64 80 96 112 128 144 160 176 192 208
Weeks in Ambient Storage
ISD Rating, mg/100 mL
0 1 2 3 4 5 6 7 8 9
0 16 32 48 64 80 96 112 128 144 160 176 192 208
Weeks in Ambient Storage
Peroxide Number
0 .5 1 1.5 2 2.5 3 3.5 4 4.5
0 4 8 12 16 20 24
Weeks in 43° C Storage
ISD Rating, mg/100 mL
0 3 6 9 12 15 18
122.5
119.0
0 4 8 12 16 20 24
Weeks in 43° C Storage
Peroxide Number
0 1 2 3 4 5
0 4 8 12
Weeks in 54° C Storage
ISD Rating, mg/100 mL
0 15 30 45 60 75 90
301.5
256.5
0 2 4 6 8 10 12
Weeks in 54° C Storage

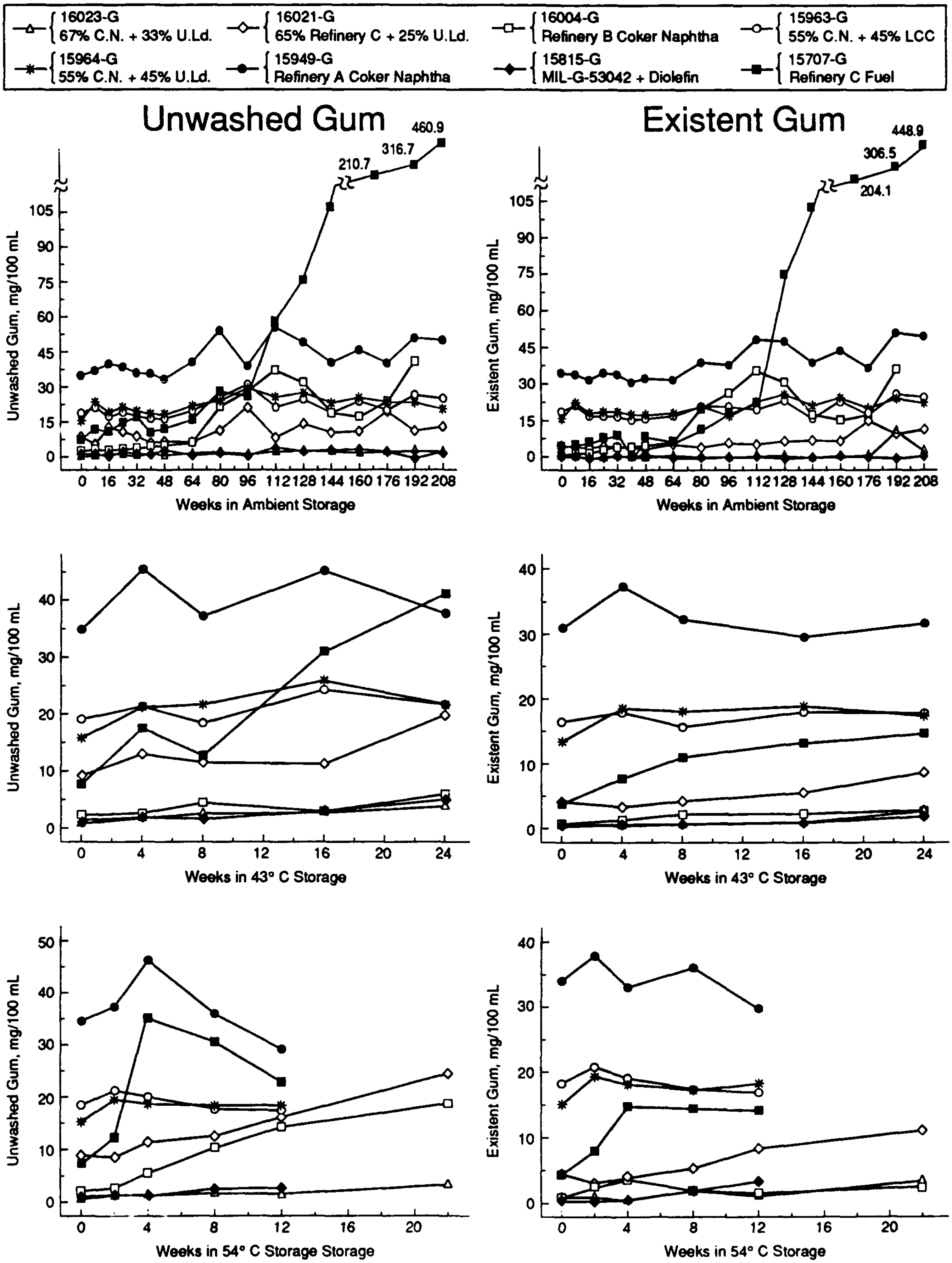
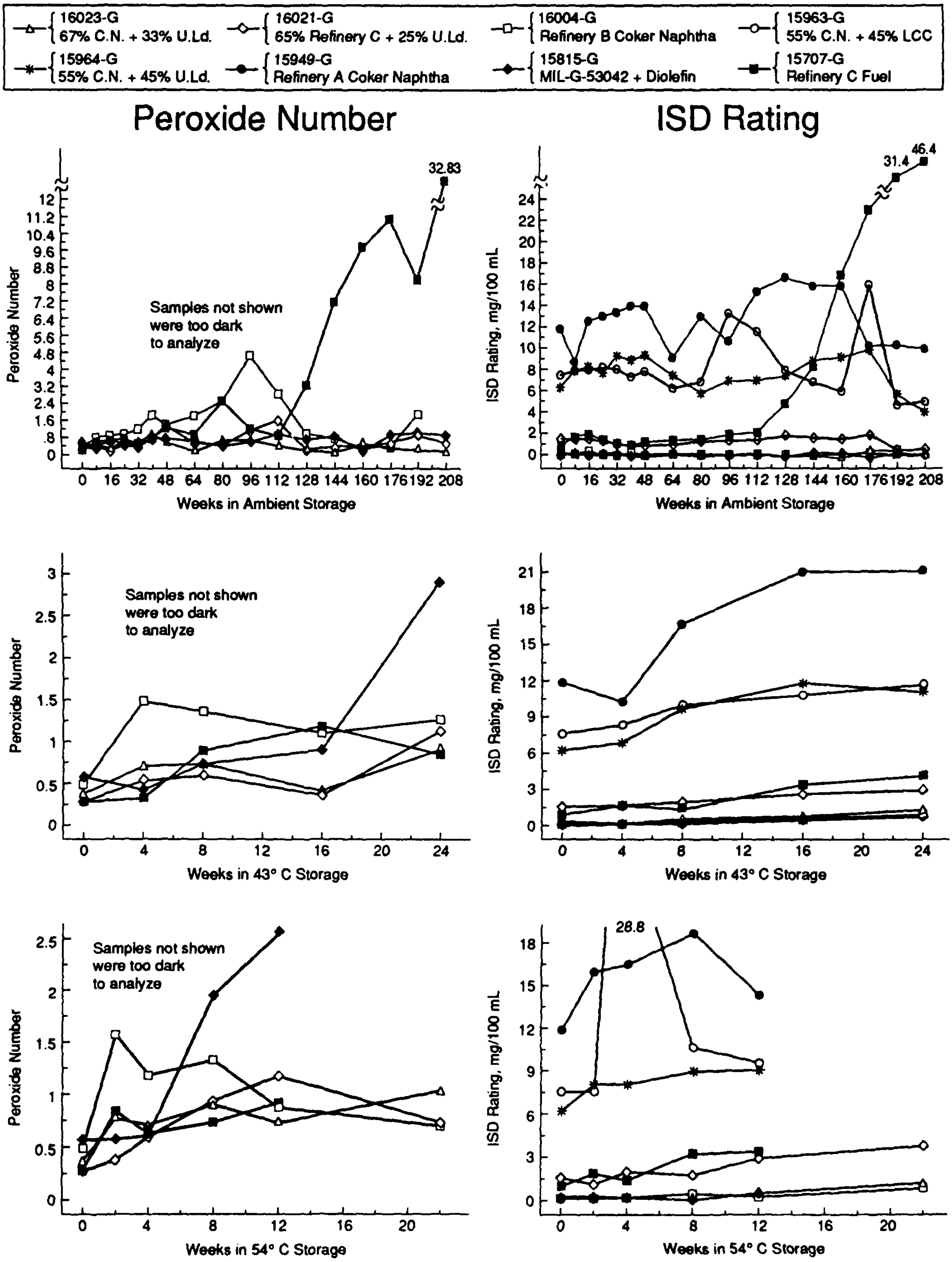


Figure E-3. **Phase III data**


16023-G 67% C.N. + 33% U.Ld.
16021-G 65% Refinery C + 25% U.Ld.
16004-G Refinery B Coker Naphtha
15963-G 55% C.N. + 45% LCC
15964-G 55% C.N. + 45% U.Ld.
15949-G Refinery A Coker Naphtha
15815-G MIL-G-53042 + Diolefin
15707-G Refinery C Fuel
Peroxide Number
ISD Rating
32.83
Samples not shown were too dark to analyze
Peroxide Number
0 .8 1.6 2.4 3.2 4 4.8 5.6 6.4 7.2 8 8.8 9.6 10.4 11.2 12
0 16 32 48 64 80 96 112 128 144 160 176 192 208
Weeks in Ambient Storage
31.4
46.4
ISD Rating, mg/100 mL
0 2 4 6 8 10 12 14 16 18 20 22 24
0 16 32 48 64 80 96 112 128 144 160 176 192 208
Weeks in Ambient Storage
Samples not shown were too dark to analyze
Peroxide Number
0 0.5 1 1.5 2 2.5 3
0 4 8 12 16 20 24
Weeks in 43° C Storage
ISD Rating, mg/100 mL
0 3 6 9 12 15 18 21
0 4 8 12 16 20 24
Weeks in 43° C Storage
Samples not shown were too dark to analyze
Peroxide Number
0 0.5 1 1.5 2 2.5
0 4 8 12 16 20
Weeks in 54° C Storage
28.8
ISD Rating, mg/100 mL
0 3 6 9 12 15 18
0 4 8 12 16 20
Weeks in 54° C Storage

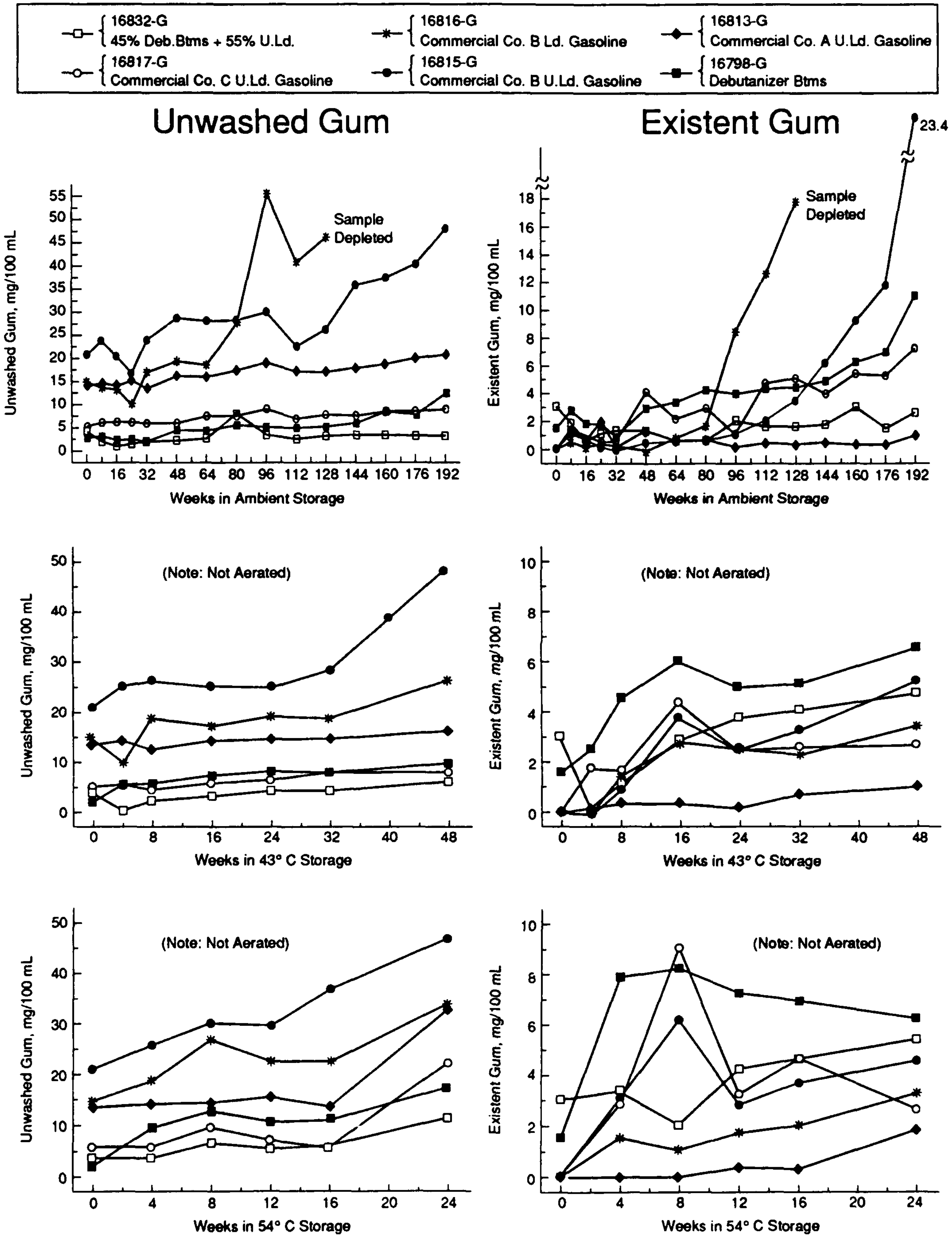
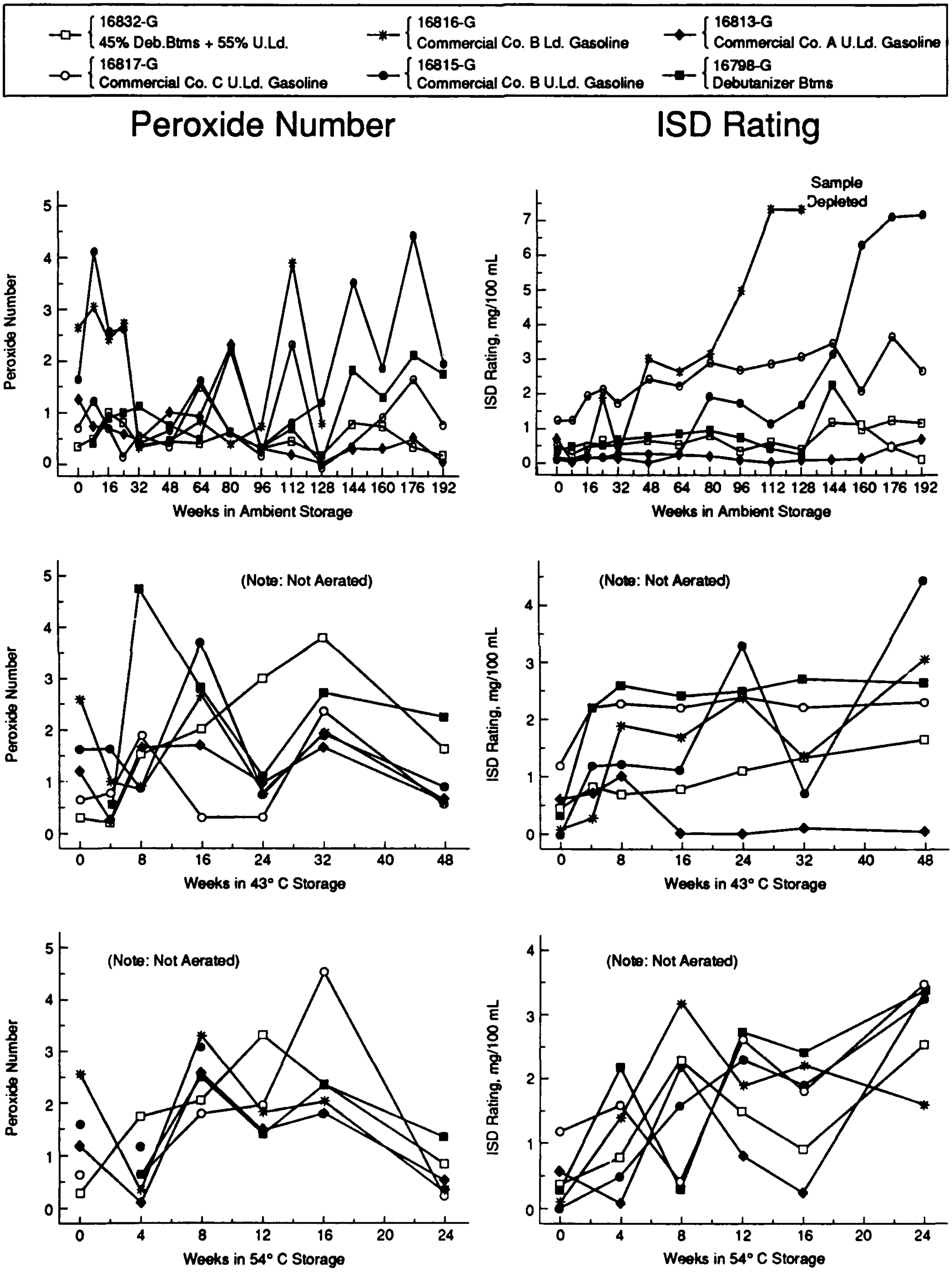


Figure E-4. Phase IV data


16832-G 45% Deb.Btms + 55% U.Ld.
16816-G Commercial Co. B Ld. Gasoline
16813-G Commercial Co. A U.Ld. Gasoline
16817-G Commercial Co. C U.Ld. Gasoline
16815-G Commercial Co. B U.Ld. Gasoline
16798-G Debutanizer Btms
Peroxide Number
ISD Rating
Peroxide Number
0 1 2 3 4 5
0 16 32 48 64 80 96 112 128 144 160 176 192
Weeks in Ambient Storage
Sample Depleted
ISD Rating, mg/100 mL
0 1 2 3 4 5 6 7
0 16 32 48 64 80 96 112 128 144 160 176 192
Weeks in Ambient Storage
(Note: Not Aerated)
Peroxide Number
0 1 2 3 4 5
0 8 16 24 32 40 48
Weeks in 43° C Storage
(Note: Not Aerated)
ISD Rating, mg/100 mL
0 1 2 3 4
0 8 16 24 32 40 48
Weeks in 43° C Storage
(Note: Not Aerated)
Peroxide Number
0 1 2 3 4 5
0 4 8 12 16 20 24
Weeks in 54° C Storage
(Note: Not Aerated)
ISD Rating, mg/100 mL
0 1 2 3 4
0 4 8 12 16 20 24
Weeks in 54° C Storage

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