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A REVIEW OF DIESEL FUEL DETERIORATION AND RELATED PROBLEMS.(U)

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A REVIEW OF DIESEL FUEL DETERIORATION AND RELATED PROBLEMS

INTERIM REPORT
AFLRL NO. 88

by

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) This report represents in essence an "overview" presented by the authors at a seminar sponsored by the U.S. Army Research Office (ARO) in April 1977 to promote basic research in the area of "Diesel Fuel Stability". This report provides a review of the general topic of fuel deterioration with primary emphasis on diesel or distillate fuels used in compression ignition engines which power the majority of Army tactical and combat.		

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vehicles. Selected field problems regarding fuel stability and related problems are presented and the status of on-going research and development programs are outlined. This information has been prepared to place in perspective the background and field problems which have prompted current research activities to detect, predict, and prevent fuel stability associated equipment failures. A selected bibliography used as the basis for the review portion of this report and as a source for additional fuel stability information has been provided.




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I. INTRODUCTION

Long term storage stability has been a requirement imposed on military fuels designed for tactical/combat environments. This requirement has been necessary because of a need to insure that fuels delivered or deployed in strategic locations will be satisfactory for use during combat operations *regardless* of the time interval between refinery production and ultimate use. This becomes very critical in relation to prepositioning of fuel stocks wherein *good* fuel quality must be maintained. Without this guarantee of maintaining fuel stability, the combat fuels could prove to be the weak link during combat operations leading to engine malfunctions, increased maintenance problems, equipment vulnerability, decreased mobility, and numerous other problems. This became obvious during the North African campaign of WW II where gasoline stored in 5-gallon Jerry cans caused serious engine problems because of inadequate stability. As a result of this, the Ordnance Corp. (and later the Army Materiel Command) sponsored research with Stanford Research Institute, Bureau of Mines, and other organizations designed to investigate the causes and/or origins for the fuel instability as related to *gasoline*. This led to the development of Military Specification, MIL-G-3056, combat automotive gasoline designed to have a storage capability of 3-5 years. An additive package was incorporated into the specification. Concurrently, the Army has conducted research to define diesel fuel stability and investigated a number of fuel stability related problems.

In an effort to promote *basic* research in the area of "Diesel Fuel Stability", the U.S. Army Research Office (ARO) sponsored a seminar at Southwest Research Institute in San Antonio, Texas in April 1977. The bulk of this report represents in essence the "overview" presented by the authors at the ARO sponsored meeting. This report provides a review of the general topic of fuel deterioration with primary emphasis on diesel or distillate

fuels used in compression ignition engines which power the majority of Army tactical and combat vehicles. Selected field problems regarding fuel stability and related problems are discussed chronologically and the status of on-going R&D programs are outlined. This information has been prepared to place in perspective the background and field problems which have prompted current research activities to detect, predict, and prevent fuel stability associated equipment failures. A selected bibliography used as the basis for the review portion of this report and as a source for additional fuel stability information has been provided^{(1-33)*}.

II. FUEL DETERIORATION

A. Definition of Storage Stability

The term "fuel stability" can be defined as the general resistance of a fuel to change.⁽²³⁾ More specifically, "fuel storage stability" is defined as the relative chemical reactivity of the fuel in terms of its tendency to form *degradation* products which cause operating problems due to *deposition* in storage, distribution systems, vehicle fuel tanks, and in the combustion system. The degradation products are usually referred to by a variety of names. Essentially, all fuels contain "gums" which are formed during the deterioration of the fuel. This "gum" is an existent material in the fuel which is found in both soluble and insoluble forms. "Soluble gum" sometimes referred to as "existent gum" is dissolved in the fuel and cannot be filtered from it. It however can be recovered by flash evaporation or thermal stressing. Since it contributes to engine deposits and is thought to be a precursor of "insoluble gum", it is undesirable. "Insoluble gum" is insoluble in the

*Superscript numbers in parentheses designate references at end of report.

fuel. It clogs fuel filters and fouls an engine's fuel injector system.^(7,10,15,16) "Insoluble gums" are sometimes referred to as "filterable insolubles".

B. Proposed Mechanisms

Oxidation has long been identified as the major process under which fuel deterioration occurs. Previous work done by the Bureau of Mines⁽¹⁴⁾ established the dependence of the rate of gum formation in gasoline on the available oxygen in the storage container. The reaction of molecular oxygen with hydrocarbons involves the formation of free radicals as intermediates.⁽¹¹⁾ Alkyl free radicals react readily with oxygen to form peroxy radicals or to yield an unsaturated compound via loss of hydrogen atoms. At high temperatures, direct reaction between oxygen and hydrocarbons occur giving rise to radical intermediates leading to oxidation via free-radical chain processes. At lower temperatures (25°C-80°C), these initiation processes are autocatalytic and involve catalysis by trace amounts of hydroperoxides. Such initiation is markedly accelerated by trace amounts of heavy metal ions.

Since storage stability is a function of autooxidation, numerous investigators have studied factors which determine the degree of storage stability and have proposed *mechanisms* by which insoluble gum or sediment is formed. One such study involving catalytically cracked distillate fuels concluded that most of the sediment is formed through oxidation of part of the aromatic thiols present in the fuel to sulfonic acids, a reaction which in the presence of air, leads to a condensation of pyrroles.⁽²⁴⁾ Another study concluded that the instability of gas oil fractions was influenced by such species as aromatic olefins, alkyl thiophenes, conjugated dienes, and pyrroles.⁽²⁵⁾ A third study involved sediment formation in distillate fuels.⁽²⁶⁾ Laboratory analysis and experimental

studies resulted in formulation of the following proposed mechanism⁽²⁶⁾ of sediment formation:

- Step 1 - The side chain oxidation of reactive hydrocarbons, nitrogen, and sulfur compounds, is catalyzed by thiols to form hydroperoxides.
- Step 2 - These partially decompose by splitting out water to form aldehydes.
- Step 3 - The aldehydes react with other hydroperoxides to form peroxyhemiacetals.
- Step 4 - The peroxyhemiacetals decompose by two reaction paths to form monomeric oxidation products by one path and condensed, esterified products of higher molecular weight by the other.

Needless to say, the difficulties in analyzing the composition of various degradation products which have very complicated molecular structures are the primary reason for not completely understanding the mechanisms of deterioration. It appears in review that most experiments dealing with fuel stability do not test *hypothesis*, but generate data for building theories.⁽¹⁸⁾

C. Contributing Factors

The stability of a particular fuel depends on factors such as crude source, refinery process, finishing operation (hydrofining, acid extraction, sweetening process, additive treatment, etc.), hydrocarbon composition, contaminants, environment, handling and use factors.⁽²³⁾ With respect to hydrocarbon composition, chemical stability decreases in the following order: paraffins, naphthenes, aromatics, olefins, and diolefins. An organic sediment, the most common evidence of instability, is

believed to result from oxidation and chemical reactions such as polymerization involving unsaturated hydrocarbons and reactive organic compounds of sulfur, nitrogen, and oxygen present in the fuel. Among the sulfur compounds, the thiophenols and substituted thiophenols are the most reactive followed by polysulfides and alkyl mercaptans. Of the nitrogen compounds, the ring substituted pyrroles and indoles are the most reactive.

Other factors which enter into the fuel deterioration process are contaminants, environment, and mode of operation (use factor). Contamination⁽¹⁹⁾ by foreign material, refinery treating agents, micro-organisms, and heavy products will degrade quality and function to induce deterioration. Rust can be an effective catalyst in the deterioration process. Trace amounts of metals such as cobalt, copper, lead, zinc, and iron can function⁽⁷⁾ once solubilized in hydrocarbons as free radical catalysts in autooxidation processes. Organic acids, either naturally-occurring or remaining during chemical refinery processes and not removed can effectively degrade fuel quality by solubilizing metals present or participating in the deterioration process. Micro-organisms, existing in water bottoms, can participate in fuel deterioration processes and generate acidic fuel-soluble reaction products. The problems of product contamination leads to distillate fuels being delivered with trace amounts or more of the heavier fuels (No. 4/5/6 Fuel Oils or crude residuum). These heavy asphaltic-type ingredients, which enhance fuel deterioration, are difficult to remove and/or separate because of the non-precise separation systems employed in refinery operations.

The fuel environment plays an important factor in fuel deterioration. Obviously, the presence of a metallic surface can function to promote autooxidation by participating as a procatalyst. Metal ions, particularly copper and cobalt, are very powerful fuel hydroperoxide decomposers and act as a

catalytic means of providing a constant source of free radicals for oxidation chain initiation. The *environment* can introduce metal ions by a variety of methods. Trace organic acids can react with metallic surfaces to produce soluble complexes. Some fuel-resistant coatings referred to as "Inorganic Zinc" have been found to produce soluble zinc complexes which in turn participate in degradation processes. Cases of fuel deterioration in *terne-plate* fuel tanks have also been reported. Here, lead complexes are formed which degrade fuel quality and stability. In laboratory storage tests, "soft glass" containers were found to *retard* fuel deterioration because of leaching out of chromate ions. Pyrex glass was found to produce no effect.⁽²⁷⁾

D. Preventative Means

Removal of dissolved oxygen and use of nitrogen inerting is one means to improve and extend fuel stability. In terms of maximizing the fuel storage stability of a given fuel in bulk storage, the following represent a listing in order of increasing effectiveness:⁽¹⁶⁾

- vented aboveground tank,
- vented underground tank,
- sealed underground tank, and
- sealed underground tank with nitrogen blanket,

by reducing contamination, temperature and availability of oxygen.

Fuel deterioration may also be retarded by the addition of additives sometimes referred to as "fuel stabilizers".⁽²⁰⁾ One type are classified as antioxidants. True *antioxidants* stabilize/retard autooxidation by preventing the accumulation of organic peroxides which accumulate as the first step in formation of soluble and insoluble gums. For many years, traditional

antioxidants such as hindered phenols and dialkyl paraphenylene diamines⁽²⁰⁾ have been used in both gasoline and middle distillates. "*Color stabilizers*" are another type which are considerably more effective in preserving fuel color. Minor components in the fuel (pyrroles, phenols, etc.) oxidize during storage to form quinoid molecules which further condense producing highly colored bodies. These color bodies increase in molecular weight until they separate out as insoluble sludge or gum. Nitrogen compounds such as tertiary amines, imidazolines and tertiary alkyl primary amines have been shown to be effective stabilizers. Metal deactivators are used to complex trace metal ions such as copper, cobalt, zinc, etc. which serve as catalysts for oxidation. The most commonly used chelating agent is N,N'-disalicylidene-1,2,-diamino propane. Dispersants are the most recent type of additives to appear on the market. Their purpose is to keep gummy insolubles and other solids dispersed as small particles so that they do not interfere in fuel injection/combustion processes. They also function in overcoming problems resulting from fuel incompatibility. Fuel incompatibility^(5,8,14) is a term used to describe the condition which exists when two or more fuels from different sources produce an insoluble residue after being mixed, even though the individual fuels themselves are relatively stable. In terms of chemical structure, dispersants are usually oil-soluble ethoxylated alkyl phenols, polyisobutylene alkylated succinimides or polyglycol esters of alkylated succinic anhydride. Alternatively, fuels can be refined for long term storage such as JP-7⁽³²⁾ or the Canadian specification 3-GP-30 fuel ("Diesel Fuel: High Stability").⁽²²⁾

III. FIELD PROBLEMS RELATED TO FUEL STABILITY

A selected group of field identified, fuel related problems have been summarized in Table 1 to better identify the extent of fuel

related problems peculiar to military fuel use situations. While the information in Table 1 with respect to date, location, problems, and primary identified cause or causes is self-explanatory, item numbers 2, 4, 5, 6, 8, 9, 10 and 12 (in Table 1) are of particular interest. These events emphasize that while bulk storage conditions and time can result in fuel stability related problems as was the case with the Whiteman AFB Missile Site stored fuel (Item No. 2, Table 1), bulk storage is not a single controlling factor under field use conditions. Fuel deterioration, filter plugging, and tank corrosion occurs in vehicle fuel tank systems as was observed at several Army Depots in 1973 (Item No. 4, Table 1). Diesel fuel systems circulate the fuel as an injector coolant during operation, breathe air containing oxygen, water vapor, etc., and are a reaction vessel of undefined composition and dimension. Under these conditions, the combined effects of thermal and storage instability of the particular fuels would create (1) acidic impurities leading to corrosion and water emulsification problems, (2) oxygenated precursors participating in oxidation-condensation polymerization reactions which degrade the quality of the fuel, and (3) combinations of contaminants which further complicate fuel quality by entrainment of rust and extraneous materials and emulsification of water which provides a continuous source for microbiological activity and deterioration of the fuel. Additionally, the use of some zinc organic complex containing, (preservative-type) lubricants in the fuel during extended vehicle storage is a source of soluble zinc contaminant which degrades fuel thermal stability. The amount of fuel left in stored vehicles is usually small compared to the fuel tank size and results in maximum environmental effects on the residual fuel as was the case at Letterkenny Army Depot (Item No. 5, Table 1). Also, in this case the bulk dispensing fuel at the manufacturing plant was of questionable quality and the preservative oil contained an acid which could react with the aluminum fuel tank to form metallic soaps both of which would

Table 1.
FUEL STABILITY RELATED FIELD PROBLEMS

Item Number	Year	Location	Problem	Primary Cause or Causes Identified
1	1965	Camp Pendleton	M60 and M48 Vehicle Fuel Injection Pump Seizures	(1) Metallurgical errors and improper plunger tolerances in overhaul of fuel injection pumps. (2) Particulate debris due to degradation of fuel improperly maintained in fuel cells aggravated problem (1) above.
2	1968	Whiteman AFB	Malfunction of Engine-Generator Sets	Organic fuel deterioration products from VV-F-800 fuel (DF-2) which had been in storage approximately 4 years.
3	1971	Red River Army Depot	M561 Gamma Goat Fuel Filler Pipe Corrosion and Filter Plugging	The lead coating on some military fuel tank filler pipes is susceptible to extensive and rapid corrosive action through a chemical process involving diesel fuel vapors and air under certain storage/use conditions. The primary cause is thought to be insufficient fuel system maintenance.
4	1973	Several Army Depots	Fuel Deterioration, Filter Plugging, and Corrosion in Vehicle Fuel Tanks	The combined effects of fuel storage instability and thermal instability on the particular diesel fuels would create (1) acidic impurities leading to corrosion and water emulsification problems, (2) oxygenated precursors participating in oxidation-condensation polymerization reactions which degrade the quality of the fuel, and (3) combinations of contaminants which further complicate fuel quality by entrainment of rust and extraneous materials, and emulsification of water which provides a continuous source for microbiological deterioration. In addition, the introducing of preservative-type lubricants (which contain zinc organic complexes) into vehicle fuel systems provides soluble zinc contaminants which degrade fuel thermal stability.
5	1975	Letterkenny Army Depot	Manufacturer Stored M60A2 Tank Fuel Deterioration-Filter Plugging	(1) Deterioration of the residual fuel in the vehicle fuel cells, during long-term storage resulting in insoluble oxidation products and corrosion of metal parts in vehicle fuel systems, caused a build-up of residue on the filters. (2) The "in house" diesel fuel used at Chrysler Detroit Tank Plant appears to be contaminated with particulate matter which could contribute to the filter plugging. (3) The preservative oil VV-L-800 contains a carboxylic acid which could react with certain metals present in the fuel system forming soaps which would contribute to the filter plugging.
6	1976	Camp Guernsey, Wyoming	M110 Self Propelled Howitzer Vehicle Fuel Filter Plugging	While diesel fuel storage and thermal stability in the fuel cell over a prolonged period of time is partially causing the filter plugging problem, the lack of tank water bottom removal and open air storage without routine preventive maintenance is also responsible.
7	1976	Yuma Proving Ground	M107 Self Propelled Howitzer Vehicle Fuel Deterioration, Tank Corrosion, and Filter Plugging	Filter plugging due to fuel deterioration and corrosion debris both of which occur in the fuel tank due to nature of random operation, heat sink use of fuel tank, and fuel's sensitivity and lack of corrosion inhibitor.
8	1976	Combat Equipment Battalion East, Europe	Vehicle Diesel Fuel Tank Rust and Corrosion	Cause not yet defined but probably due to lack of adequate preservation.
9	1977	Fort Riley, Kansas	M60A1 Tank Engine Starvation due to Filter Plugging	While diesel fuel in use at the time was of marginal to poor stability, primary cause of filter plugging was due to microbiological debris.
10	1977	California National Guard Unit	Gamma Goat Fuel Tank Filler Pipe and Cap Corrosion	Corrosion of fuel filler pipe and cap of similar vehicles are thought to be due to a combination of lack of sufficient corrosion inhibitors in a fuel tank system breathing moisture and carbon dioxide containing air and exposed to daily temperature extremes (including direct sun exposure) over extended periods of time without adequate preventive maintenance.
11	1977	Fort Hood, Texas	M60A1 Tank Engine Fuel Filter Plugging	Presence of microbiological debris and fuel deterioration products identified. Fuel system maintenance and fuel treatment identified as probable cause.
12	1977	Fort Lewis, Washington	M551 Sheridan Tank Fuel Filter Plugging	Cause not yet defined, however, equipment improvement request to facilitate complete draining of fuel tank water bottoms was recommended.

cause filter plugging when the vehicle was placed in use if the tank was not thoroughly cleaned out prior to field fueling and placing in operation. Generally, the storage of a vehicle fuel system is assumed to be adequate for short periods of time if drained of most fuel and a *preservative* was added. Complete fuel tank drainage is not usually possible due to fuel tank design. This lack of ability to completely drain a fuel tank *also* means that the water bottoms cannot be drained completely from the fuel tanks. Microbiological activity at the fuel-water interface can result in microbiological debris and fuel oxidation products plugging filters as was the case at Fort Riley, Kansas and probably at Fort Lewis, Washington (Item Nos. 9 and 12, respectively, Table 1). Figures 1 and 2 are photographic reproductions of microbiological debris found in fuel systems at Fort Riley, Kansas (Item No. 9, Table 1). Evaluation of the fuel system debris from Fort Riley by the U.S. Army Natick Research and Development Command has indicated the presence of a yeast tentatively identified as *candida humicola* and a gram negative bacterium.

In the case of vehicle overhauls at Army depots, short storage periods may not exist thereby requiring more stringent fuel tank condition controls. While the total standard time including shipment of a vehicle from an operating unit to a depot, time awaiting overhaul at the depot, and time to overhaul ranges from 7.1 to 10.1 months for the M113A1 and M-88 tank, respectively, actual time has been estimated at 68.9 and 69.7 months with regard to the same respective vehicles based on a recent Comptroller General's report.⁽³⁴⁾

In some cases such as at Camp Guernsey, Wyoming (Item No. 6, Table 1), combined effects of poor fuel stability, continued intermittent operation, contamination, and lack of preventative maintenance (such as draining and cleaning the fuel tank yearly) have led to severe fuel filter plugging, an example of

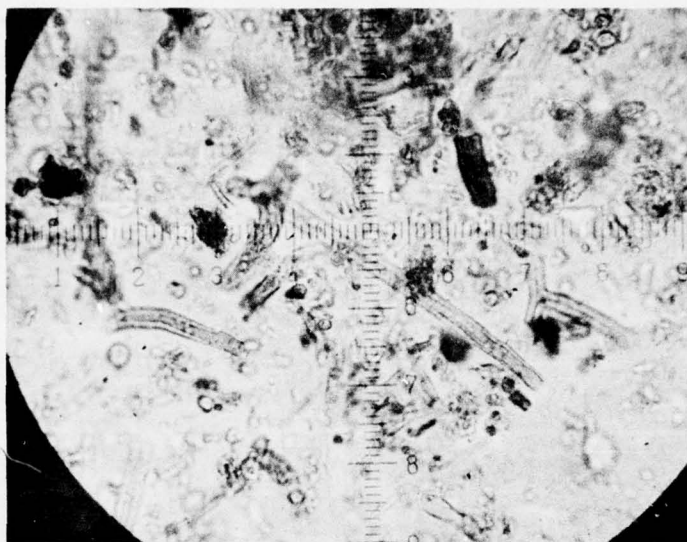


FIGURE 1. PHOTOGRAPH OF MICROBIOLOGICAL DEBRIS ON PRIMARY FUEL FILTER FROM ONE FORT RILEY M60A1 TANK

(1.4 μm /scale division, wet sample, oil wetted lens.
970X, M60A1 Tank USA #09A05772)

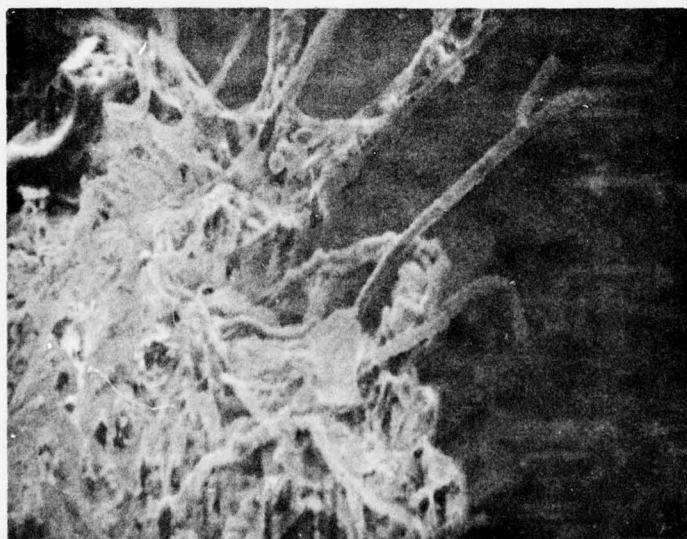


FIGURE 2. SEM OF M60A1 ENGINE SERIAL NO. 15554 SECONDARY FUEL FILTER RESERVOIR PARTICULATE SAMPLE

(Magnification, 1000X; sample was gold fluxed)

which is shown in the photograph in Figure 3. Both the difficulty in cleaning this type of fuel tank and fuel conservation requirements contribute to reduced mandatory draining and cleaning of fuel tanks as routine maintenance requirements. In the case of European POMCUS (Prepositioned Overseas Materiel Configured in Unit Sets) fuel tank problems (Item No. 8, Table 1), the long storage periods (one to four years) even under controlled humidity can result in fuel storage related problems if preventative measures (such as the use of stability additives under development and fuel condition monitoring) are not taken. The extent to which a fuel tank is drained, the quality of the residual fuel, the presence of water, the effectiveness of preservative-oil applications, etc. combine to determine the future residual fuel quality and fuel tank condition. In the case of storing fully fueled equipment, an impending requirement for POMCUS equipment, even more stringent preventative measures will be required to avoid fuel and fuel tank deterioration related problems. A constant temperature environment does eliminate the fuel tank breathing associated with daily high-low temperature variation causing cycling of the tank fuel/vapor temperature causing vapor escape at high temperature and air entrance into the tank during fuel/vapor cooling. Corrosion of fuel filler pipe and cap as in Figure 4 (and Item No. 10, Table 1) is thought to be due to a combination of lack of sufficient corrosion inhibitors in a fuel tank system breathing moisture, oxygen, and carbon dioxide containing air and exposed to daily temperature extremes (including direct sun exposure) over extended periods of time without adequate preventative maintenance such as tank draining and cleaning.

IV. TECHNOLOGY FOR PREDICTIVE APPROACHES

A. Past Efforts

A considerable amount of work has been performed to develop

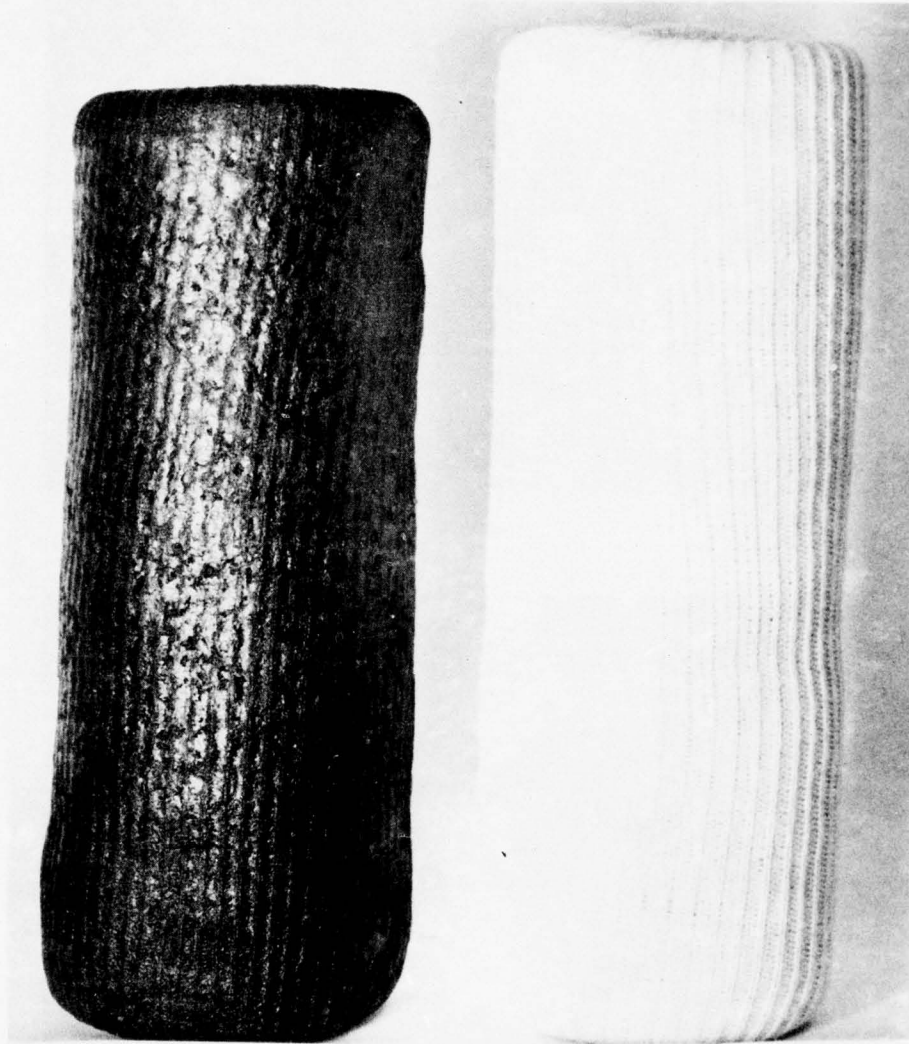
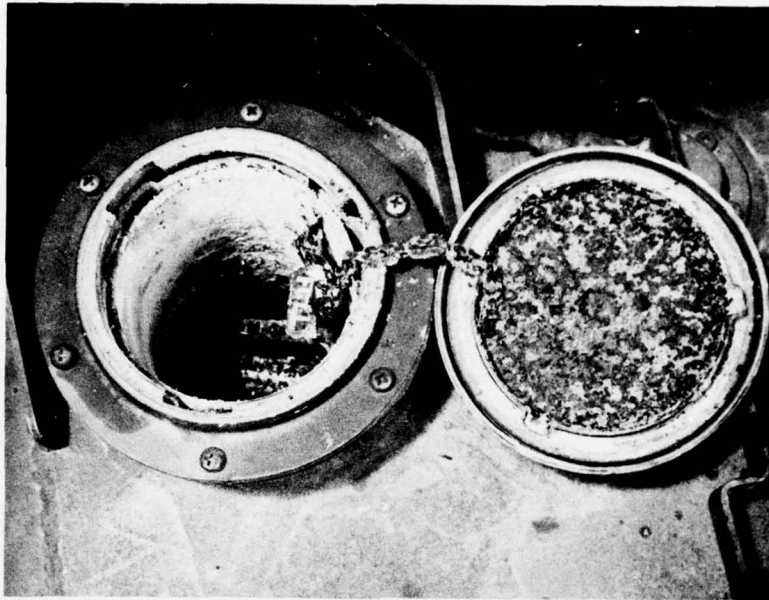
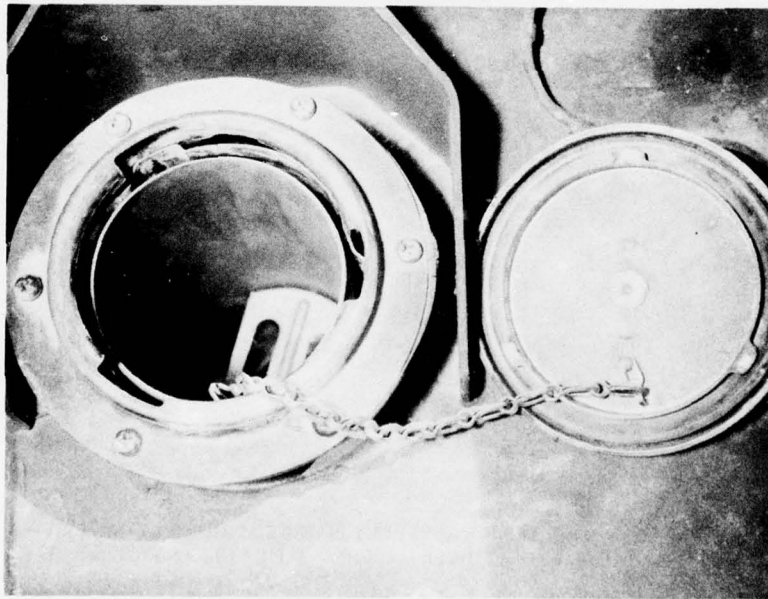


FIGURE 3. COMPARISON OF A SEVERELY PLUGGED PRIMARY FUEL FILTER FROM AN M110 SP VEHICLE (#12FH64) WITH A CLEAN FILTER



Severely Corroded



Non-Corroded

FIGURE 4. COMPARISON OF CORRODED FUEL TANK FILLER PIPE AND CAP OF IMPROPERLY STORED M561 GAMMA GOAT WITH A NON-CORRODED FILLER PIPE AND CAP

tests which predict the storage stability of fuels. A large variety of tests have been used or are in use for evaluating fuel stability. These tests are referred to as accelerated aging tests. Twenty-six different methods were tabulated in a presentation by MacDonald and Jones.⁽³¹⁾ A large range or variety of test conditions and methods of evaluating results are employed, some of which have been shown to relate directly to fuel in actual storage under certain correlated conditions of storage. While time and temperature are accepted variables in accelerated tests, the variation in containers, conditions, and especially in the method of sample evaluation gives a tremendous variety, including, for example:

Condition	Sample Evaluation
16 hr @ 98.9°C (210°F), vented quart bottle	Solids and color No. 3 porosity crucible
16 hr @ 98.9°C (210°F), vented quart bottle	Solids and color of medium porosity crucible
20 hr @ 100°C (212°F), air aging in test tube	Discoloration of filter paper
Variable time @ 37.8°C (100°F) or 93.3°C (200°F), pumped through unit type injector	Time to injector sticking
16 hr @ 90.6°C (195°F), steamed, aged, and resteamed	150 mesh screen clogging
90 min @ 148.9°C (300°F), air aging in test tube	Discoloration of filter paper
4 wks @ 60°C (140°F), unstoppered glass bottle	Solids on asbestos mat
42 hr @ 82.2°C (180°F), air agitation in beaker	Solids on medium porosity crucible
Various	Inorganic sediment, organic sediment, and soluble gum

Because of the time involved and fuel quantities (for bulk storage), actual long-term tests are very expensive and pro-

hibitive. Additionally, progress in determining causes of fuel deterioration would be slow if long-term tests were used because of the time involved. The Navy-CRC Barge Storage Program⁽²⁸⁾ conducted in the 1950's to determine the scale-down factor from barge to bottle or drum-storage provided data indicating the usefulness of storage @ 43.3°C (110°F) as a proxy variable for long-term storage. With the accumulation of additional data, most researchers have accepted the results of aging fuels at 43.3°C as consistent with those obtained under actual storage conditions. Bottle storage at 43.3°C for 13 weeks is reported to be approximately equivalent to either drum or bottle storage at ambient temperatures for one year.^(6,12,14,18) Although the American Society for Testing and Materials (ASTM) has accepted several accelerated tests for evaluating petroleum products, only the "Test for Stability of Distillate Fuel (ASTM D-2274-74)" is directly applicable to distillates.⁽³³⁾ In this test method a measured volume (350 ml) of filtered fuel is aged at a high temperature of 95°C (203°F) while oxygen is bubbled (31/hr) continuously through the sample. After aging (16 hr) and cooling, the total amount of insoluble matter formed is determined:

$$A = (B + C)/3.5$$

where

A = Total insolubles, mg/100 ml

B = Weight of filterable insolubles, mg

C = Weight of adherent insolubles, mg

The ASTM D-2274-74 accelerated stability technique is currently specified in VV-F-800b as a prediction of storage stability for bulk fuel deliveries at the time of procurement.

Two additional test methods are used specifically as a measure of contamination:

- ASTM D2276 test modified to use 1.2 μ m filters to determine particulates
- ASTM D381 test for existent gum

These same types of methods have proved useful in determining "How Stable is Diesel in Storage?" in a two-year, 100-barrel, aboveground steel tank storage program using four diesel fuels meeting Federal Specification VV-F-800a.⁽²¹⁾

Accelerated test results can be related to long-term storage results and can indicate the less stable fuels. However, absolute test methods to predict fuel quality at specific time intervals under all types of storage conditions have yet to be developed. Basic research into the mechanism of diesel fuel deterioration has been attempted at the U.S. Army Fuels and Lubricants Research Laboratory in an effort to better define the chemical composition parameters and their interrelation in the formation of deleterious degradation products. Strict compositional relationships have thus far been unsuccessfully developed and this has resulted in more emphasis being placed on the development of empirical relationships.

B. Current Program

One approach in terms of new predictive methodologies being considered by the Army has involved use of a dynamic oxidation autoclave wherein maximum aeration of a liquid under pressure occurs.⁽²⁴⁾ The assessment of oxidation is accomplished by measuring the dipole moment of reaction products. This estimated dipole moment which is termed "Polarization Index" is computed from relatively simple measurements of dielectric

constant and refractive index before and after the oxidization environment. The initial experiments involved use of automotive gasoline with test conditions being 100°C for 24 hours. The validity of this approach was confirmed by defining a significant correlation between the "Polarization Index" and oxygen consumption; these two parameters being determined independently of each other. A series of tests conducted on 42 gasolines revealed those having high olefin content to be more prone to oxidation. This technique is now being applied to diesel fuels as a possible predictor of storage stability.

The current program at the U.S. Army Fuels and Lubricants Research Laboratory is essentially four-fold:

- a. develop field test for fuel quality,
- b. develop field test for predicting fuel stability,
- c. develop information input for possible stability additive specification for Army depot use, and
- d. define fuel involvement in vehicle fuel tank/filler pipe corrosion,

with primary interest in items (a) and (b). This project was initiated in late 1976 using refinery and Army Depot diesel fuel samples by subjecting the sample fuels to a battery of tests summarized in Table 2, some of which are classified as fuel quality tests while the others were predictive in nature. Based on correlative data, potential field tests are yet to be fully defined and evaluated. Concurrently, an effort using the same test fuels and test methods has been initiated to supply information in support of items (c) and (d) using commercially available multipurpose additive packages and vehicle fuel system components, respectively.

Table 2.
ANALYTICAL AND ACCELERATED STABILITY TEST METHODS

Test No.	Description	Test No.	Description
(1)	Steam Jet Gum	(16)	Heat Treat Filterability Ratio Test
(2)	Water and Sediment	(17)	Chromic Acid Number Test
(3)	Copper Corrosion	(18)	Cold Room (2°C) Storage (5-gal.)
(4)	NACE Steel Corrosion	(19)	43.3°C (110°F) Storage (650-ml)
(5)	Color		<ul style="list-style-type: none"> • Pyrex Container Vented • Flint Glass Container Vented
(6)	Particulates <ul style="list-style-type: none"> • 1.2μ • 0.45μ 	(20)	79.4°C (175°F) Storage Test (105-ml) (sample bottles without caps analyzed at 1,3, and 7-day duration)
(7)	Filterability Ratio		<ul style="list-style-type: none"> • Color • Light Scattering • Light Absorbance • Silica Gel Dark Zone • Steam Jet Gum • Particulates (1.2μ)
(8)	Light Scattering		
(9)	Light Absorbance		
(10)	Silica Gel Dark Zone Test		
(11)	Accelerated Stability (ASTM D2274) <ul style="list-style-type: none"> • Standard Method • Modified • Filtrate Analysis 	(21)	148.9°C (300°F) Storage Test (55-ml) (Pyrex tubes with no caps for 90-minute duration)
(12)	Recycle Fuel Coker		<ul style="list-style-type: none"> • Test Tube Nos. 1 and 2 • Color • Light Scattering • Light Absorbance • Silica Gel Dark Zone • Particulates (1.2μ)
(13)	JFTOT		
(14)	Field Modified JFTOT		
(15)	Heat Treat Light Scattering Test		<ul style="list-style-type: none"> • Test Tube No. 3 • Steam Jet Gum

V. PERSPECTIVE FOR THE FUTURE

Means of testing fuel quality, predicting fuel stability, and preventing fuel related material problems in the field continue to be improved and made more viable. Basic research to better define the mechanisms involved in diesel fuel stability will contribute to this effort. The "energy crisis" and manpower cuts with their resultant effect on maintenance practices mandate better field methods of detecting and preventing fuel and fuel related material defects that develop in the field. Fuel stability mechanisms should be viewed in their broadest framework so as to include quantity (both large and small), term (both short and long), container (both bulk and vehicle), and environment (both external and internal components). This viewpoint will best serve both short and long term material readiness as it is affected by fuel and fuel storage stability.

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