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Final Report

# USATHAMA

U.S. Army Toxic and Hazardous Materials Agency

## Laboratory Tests to Determine the Chemical and Physical Characteristics of Propellant-Solvent-Fuel Oil Mixtures

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Prepared by

TENNESSEE VALLEY AUTHORITY  
NATIONAL FERTILIZER &  
ENVIRONMENTAL RESEARCH CENTER  
Muscle Shoals, Alabama 35660  
Under TVA Contract No. TV-79416

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Prepared for

U.S. Army Toxic and Hazardous Materials Agency  
Aberdeen Proving Ground (Edgewood Area)  
Maryland 21010-5401  
USATHAMA Project RI6.01.09.21

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FINAL REPORT

LABORATORY TESTS TO DETERMINE THE CHEMICAL AND PHYSICAL  
CHARACTERISTICS OF PROPELLANT-SOLVENT-FUEL OIL MIXTURES

Compiled by

V. M. Norwood, Ph. D.  
Division of Research

D. J. Craft  
C. E. Breed - Project Manager  
Division of Chemical Development

February 1990

Prepared by

Tennessee Valley Authority  
National Fertilizer & Environmental Research Center  
Muscle Shoals, Alabama 35660

Prepared for

United States Army Toxic and Hazardous Materials Agency  
Aberdeen Proving Ground (Edgewood Area)  
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The propellant studied during the six-month course of this project was a smokeless-grade nitrocellulose containing 13.15% nitrogen by weight. A series of laboratory tests were conducted to evaluate the physical and chemical characteristics, as well as the chemical compatibility of, nitrocellulose-solvent and nitrocellulose-solvent-No. 2 fuel oil mixtures. The solvents initially studied were acetone, butyl acetate, ethyl acetate, tetrahydrofuran, and 2-butanone. An economic analysis was also performed to compare the cost of burning nitrocellulose-solvent-No. 2 fuel oil mixtures versus the cost of burning nitrocellulose-No. 2 fuel oil mixtures as supplemental fuels. The combined results of the laboratory tests and the economic analysis indicated that only the nitrocellulose-No. 2 fuel oil mixtures should be pursued further as potential supplemental fuels for use in Army industrial combustors.



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## EXECUTIVE SUMMARY

The objective of this project was to conduct a preliminary evaluation of the feasibility of dissolving waste propellant in an appropriate solvent and blending this solution with No. 2 fuel oil to produce a supplemental fuel for use in the United States Army's industrial combustors. This project represents a logical extension of a previous program conducted by the United States Army Toxic and Hazardous Materials Agency (USATHAMA) to develop methods and procedures for utilizing waste explosives (primarily TNT and Composition B) blended with a solvent and fuel oil for use as a supplemental fuel. A smokeless-grade nitrocellulose (13.15% by weight nitrogen content) was used during this project as an appropriate substitute for an actual propellant sample. As specified by USATHAMA, this project only had a six-month time frame for completion. It was not possible to obtain an actual propellant sample within this period of time.

An extensive series of laboratory tests were conducted to evaluate the physical and chemical characteristics, as well as the chemical compatibility, of nitrocellulose-solvent and nitrocellulose-solvent-No. 2 fuel oil mixtures. Based on the results obtained from these laboratory tests, an economic analysis was performed using the nitrocellulose-solvent-No. 2 fuel oil mixtures which possessed the most desirable physical and chemical characteristics for use as a supplemental fuel.

The physical characteristics of nitrocellulose-solvent and nitrocellulose-solvent-No. 2 fuel oil mixtures were evaluated by performing laboratory tests to measure the dilution ratios, densities, and viscosities of these solutions. In general, nitrocellulose is soluble in any solvent that contains a polar group. Based on this fact and the results of an extensive literature search, acetone, ethyl acetate, 2-butanone, tetrahydrofuran, and butyl acetate were included in this phase of the project as potentially useful solvents for nitrocellulose.

The chemical characteristics of nitrocellulose-solvent and nitrocellulose-solvent-No. 2 fuel oil mixtures were evaluated by performing laboratory tests to measure the flash points, fire points, and heats of combustion of these solutions. However, only acetone, ethyl acetate, and butyl acetate were included as potentially useful solvents for nitrocellulose in this phase of the project. The decision to eliminate tetrahydrofuran and 2-butanone from further tests was based on preliminary results from the economic analysis, health risk data, and consultations with USATHAMA personnel.

The chemical compatability of selected nitrocellulose-solvent and nitrocellulose-solvent-No. 2 fuel oil mixtures was assessed by a thermal analysis technique known as differential scanning calorimetry. This technique showed that the chemical stability of the nitrocellulose was not affected by dissolving it in a solvent and blending this solution

with No. 2 fuel oil. In addition, qualitative observations were made of nitrocellulose-solvent and nitrocellulose-solvent-No. 2 fuel oil solutions to determine if any color changes, separation of phases, or precipitation might occur over the six-month time frame of this project.

The economic analysis indicated that acetone was the least expensive solvent for dissolving the nitrocellulose. However, the economic analysis also clearly showed that burning nitrocellulose-solvent-No. 2 fuel oil mixtures as supplemental fuels would be prohibitively expensive as a process for disposing of large amounts of waste propellants. On the other hand, another economic analysis did show that burning a slurry of nitrocellulose in No. 2 fuel oil as a supplemental fuel would be a cost-effective alternative to the process discussed in this report.

Four appendices are included in this report:

- A. ASTM Standard Procedures (details of the experimental procedures),
- B. Supplemental Literature References (complete list of useful articles identified in the literature search but not cited in the text of the report),
- C. Calculations for Table 12 (economic analysis of nitrocellulose-acetone-No. 2 fuel oil mixtures),

D. Calculations for Table 13 (economic analysis of nitrocellulose-No. 2 fuel oil mixtures).

The major conclusion of this project and a recommendation for additional studies, based on the chemical and physical characteristics tests, the chemical compatability tests, and the economic analysis of the nitrocellulose-solvent and nitrocellulose-solvent-No. 2 fuel oil mixtures are as follows:

1. Acetone, as well as being the best technical solvent, is also the least expensive solvent for nitrocellulose. However, burning a nitrocellulose-acetone-No. 2 fuel oil solution as a supplemental fuel for the Army's industrial combustors would be prohibitively expensive. The main technical drawback in this process, which also contributes to the expense, is the fact that only relatively small amounts (approximately 2-3 weight percent) of nitrocellulose could be incorporated in the acetone-No. 2 fuel oil mixture without increasing the viscosity of the resulting nitrocellulose-acetone-No. 2 fuel oil solution beyond the maximum value which a conventional oil burner could conceivably handle.

2. Future work should include a study of the physical and chemical characteristics, as well as the chemical compatability of propellant-No. 2 fuel oil mixtures. This recommendation for additional work is based on the fact that the economic analysis of nitrocellulose-No. 2 fuel oil mixtures included in this report clearly showed that burning such a

mixture, which would be in the form of a slurry since nitrocellulose (propellant) is not soluble in No. 2 fuel oil, would not only be cost-effective but would also dispose of significant metric ton amounts of nitrocellulose (propellant) per year. The amount of waste material which could be disposed of per year depends both on the weight percent content of nitrocellulose (propellant) in the slurry and the size of the boiler used for the combustion process.

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ABSTRACT

The military currently has an inventory of approximately 158,000 metric tons of propellants, explosives, and pyrotechnics, with a total of 249,000 metric tons projected by the year 1993. This inventory includes obsolete conventional munitions and waste propellant generated during the manufacturing process. The current alternatives to storage are open-air burning, open-air detonation, or incineration to slowly reduce the inventory of these materials. The United States Army Toxic and Hazardous Materials Agency (USATHAMA) is currently coordinating a program to assess the feasibility of utilizing propellants dissolved in an appropriate solvent and further blended with fuel oil as supplemental fuel for Army industrial combustors. This report discusses the results from the initial phase of this program.

The propellant studied during the six-month course of this project was a smokeless-grade nitrocellulose containing 13.15% nitrogen by weight. A series of laboratory tests were conducted to evaluate the physical and chemical characteristics, as well as the chemical compatibility of, nitrocellulose-solvent and nitrocellulose-solvent-No. 2 fuel oil mixtures. The solvents initially studied were acetone, butyl acetate, ethyl acetate, tetrahydrofuran, and 2-butanone. An economic analysis was also performed to compare the cost of burning nitrocellulose-solvent-No. 2 fuel oil mixtures versus the cost of burning nitrocellulose-No. 2 fuel oil mixtures as supplemental fuels. The combined results of the laboratory tests and the economic analysis indicated that only the nitrocellulose-No. 2 fuel oil mixtures should be pursued further as potential supplemental fuels for use in Army industrial combustors.

## 1. INTRODUCTION

The military currently has a large inventory of acceptable propellants which are obsolete due to changes in the weapon systems for which the propellants were originally produced. Additional quantities of waste propellants, i.e., propellants that do not conform to ballistic, chemical, or physical specifications, are generated during the normal process of manufacturing these materials. For example, according to the Environmental Conference proceedings of the "Hazardous Waste Minimization Interactive Workshop" sponsored by the Army Materiel Command in November 1987, 158,000 metric tons of obsolete conventional munitions are in the demilitarization inventory with a total of 249,000 metric tons projected by the year 1993.

Currently available options for disposing of obsolete or out-of-specification propellants are open-air burning, open-air detonation, or incineration.<sup>1,2</sup> For example, at the Radford Army Ammunition Plant alone, 88 metric tons of solvent-based propellants (single-, double-, or triple-base) are slowly being disposed of by open-air burning or incineration. However, these options are being severely constrained due to increased pressure from local, state, and national environmental groups and agencies.

The United States Army Toxic and Hazardous Materials Agency (USATHAMA) is currently conducting a program to develop methods and procedures for utilizing waste explosives (primarily TNT and Composition



B) blended with solvents and fuel oil as a supplemental fuel for use in Army industrial combustors.<sup>3</sup> As a logical extension of this program, USATHAMA is now sponsoring a program to develop methods and procedures for utilizing waste propellants (nitrocellulose-based materials) blended with solvents and fuel oil as supplemental fuel for use in Army industrial combustors. This report will describe the results from an extensive series of laboratory tests conducted to evaluate the technical merit of using waste propellants as fuel oil supplements. These laboratory tests determined the chemical and physical characteristics, as well as the chemical compatibility, of supplemental fuels composed of a smokeless-grade nitrocellulose dissolved in an appropriate solvent and further mixed with No. 2 fuel oil.

## 1.1 PHYSICAL AND CHEMICAL CHARACTERISTICS OF CELLULOSICS

Since nitrocellulose is a cellulose derivative and its solid structure strongly resembles the cellulose from which it is derived, neither the chemical nor the physical characteristics of nitrocellulose can be understood without some knowledge of the chemical and physical characteristics of the parent material. Consequently, the following sections describe some of the concepts regarding the chemical and physical characteristics of nitrocellulose which are, in fact, little more than derivatives of similar concepts developed previously for cellulose.

### 1.1.1 Physical Characterisitics

Cellulose is the structural material of the living cells of plants. Cellulose is found in several very diverse forms corresponding to the different purposes it must fulfill in the cell walls of plants, but with certain exceptions it always has the same peculiar physical characteristic of being fibrous. Two types of cellulose fiber which are important in the manufacture of nitrocellulose are woodpulp fiber and cotton linters.

#### 1.1.1.1 Woodpulp Fiber

Woodpulp is now extensively used for the preparation of nitrocellulose and other cellulose derivatives. It is the fibrous residue remaining after the treatment of disintegrated wood with a hot solution of either calcium bisulfite or sodium hydroxide. The "sulfite pulp" obtained by the calcium bisulfite treatment provides a purer form of cellulose than can be obtained from the treatment with sodium hydroxide. Early attempts to prepare nitrocellulose from woodpulp fiber were plagued with many difficulties, mainly caused by the high pentosan content of the fiber. For example, attempts to introduce nitrate groups onto the woodpulp cellulose backbone with nitrating acids of high water content resulted in hydrolysis of the pentosans without the desired result of nitration. Furthermore, a series of insoluble by-products were also formed. Moreover, attempts to use more concentrated nitrating acids resulted in the formation of nitropentosans. These substances were soluble in the solvents employed for producing nitrocellulose-containing films and resulted in films with unsatisfactory physical properties and unstable chemical properties. Eventually, a certain pentosan content was found to be tolerable and, as stated above, woodpulp is now extensively used for manufacturing nitrocellulose.

#### 1.1.1.2 Cotton Linters

Normal cotton fiber is too valuable to use for manufacturing nitrocellulose. Although cotton waste (the scrap material from weaving and spinning) is sometimes used to make nitrocellulose for military purposes, and "cops" (the ends of yarn which are left on the bobbins) are still the best material for making a special type of nitrocellulose which is incorporated into many industrial explosives, the only variety of cotton used for conversion into nitrocellulose and other esters or ethers on an industrial scale is linters.

The normal cotton hair has a length which averages between 2 to 5 cm. The linters are the material remaining on or attached to the cotton seed after the longer hairs have been removed. The length of the cotton linters are much shorter than that of the normal cotton hairs, i.e., the linters average between 0.05 to 0.50 cm. The linters weigh anywhere from 10 to 12% of the weight of the seed. Under the microscope, linters are observed to consist of two main types; one normal, like long-fibered cotton hairs, having a fairly wide canal and many convolutions, and a second kind which is generally rather narrower and has a relatively narrower canal and no convolutions. These differences affect the end-products manufactured from the nitrocellulose prepared from cotton linters. For example, one of the requirements in the manufacture of industrial-grade nitrocellulose which is often very difficult to obtain is that its solutions should be free from undissolved or swollen

particles. Frequently, if the physical structure of the cotton linter is abnormal, such abnormality becomes the source of some of the "haze" or other lack of clarity in solution.

#### 1.1.1.3 Analysis of Cellulose Fibers

The physical changes which accompany the nitration of cellulose fibers has been followed by scanning electron microscopy (SEM)<sup>4</sup>. For instance, the surface of the cotton linters and woodpulp fibers showed a greater porosity and degradation of their structure after nitration than they did before. Furthermore, cotton linters were found to be less damaged than woodpulp fibers.

The typical nitrocellulose sample derived from cotton linter is a long tube which is made up of fibrils coiled into a helix (Figure 1A). The surface of this tube shows smooth-edged pores suggesting partial solvation of the cellulose during nitration. On the other hand, all nitrocellulose fibers derived from wood have a flattened ribbon shape with pits or pores which are also typically seen in woodpulp cell walls (Figure 1B, Hercules Grade C, Type 1). The surface of the nitrocellulose fibers derived from woodpulp also suggests partial solvation during nitration, with subsequent rapid drying.

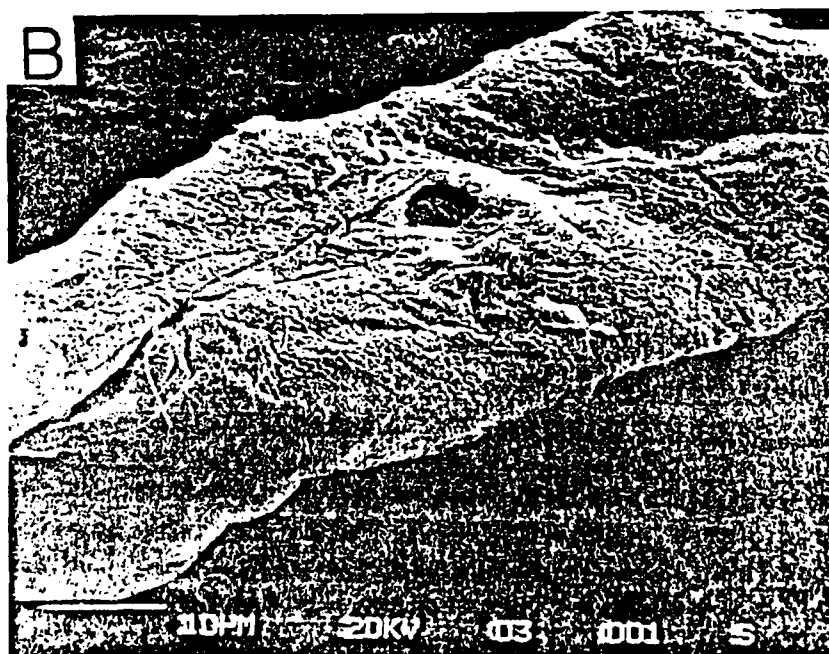
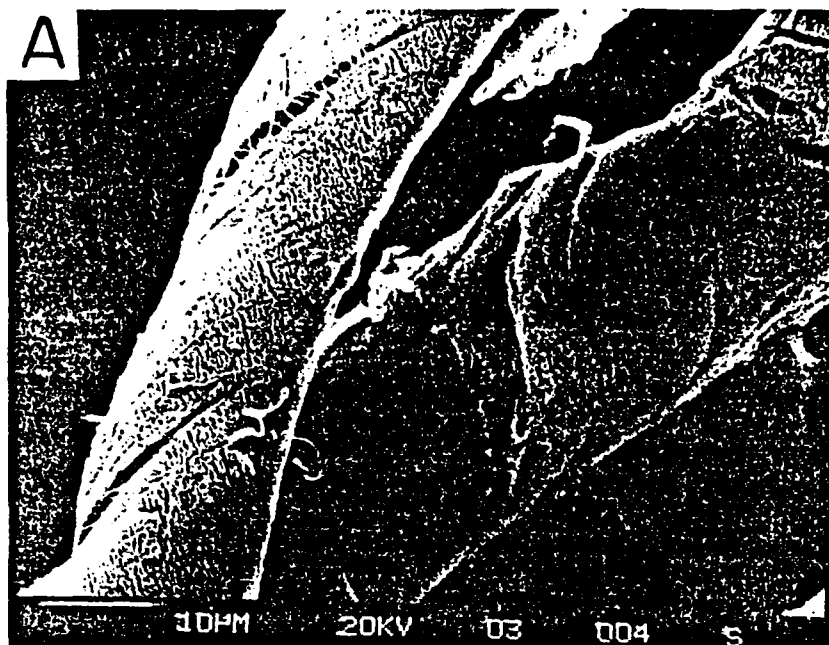


Figure 1. Scanning Electron Micrographs of Nitrocellulose Samples:  
 (A). Nitrocellulose Derived from Cotton Linters,  
 (B). Nitrocellulose Derived from Woodpulp.

### 1.1.2 Chemical Characteristics

#### 1.1.2.1 The Reaction of Cellulose with Nitric Acid

The formation of inflammable materials by the action of concentrated nitric acid on carbohydrates was first observed in 1833 by Braconnot, who obtained very impure products from cotton, starch, woodfiber, etc., which he called "xyloidines". A few years later, Pelouze made more definitive observations on the same subject. However, the first chemist to fully recognize the technical importance of the reaction of nitric acid with cellulose, as well as the first to prepare relatively pure cellulose nitrates was Schonbein. Schonbein patented the process of manufacturing a nitrated material from cotton by treating it with a mixture of nitric and sulfuric acids in 1846. The early detailed history, with ample quotations of significant passages from the original papers of Braconnot, Pelouze, and Schonbein, has been given by MacDonald<sup>5</sup>. In addition, the part played by nitrocellulose in the history of propellants and explosives has been summarized in detail by Marshall<sup>6</sup>.

The chemical reaction which converts cellulose to nitrocellulose is actually not a nitration but an esterification reaction. Typical nitrocelluloses are high molecular weight ( $10^5$ - $10^6$  g/mole) polymer chains composed of anhydroglucose units, each containing up to three nitrate groups. Two such units for fully nitrated cellulose are shown in Figure 2.

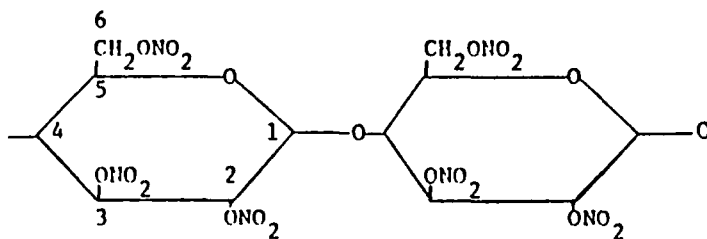


Figure 2. Fully Nitrated (14.15% nitrogen) Nitrocellulose

In each glucose residue of the cellulose chain there are three hydroxyl ( $-OH$ ) groups, two secondary and one primary, which theoretically could result in the formation of three or more definite compounds corresponding to the successive nitration of each type of hydroxyl group in each residue. In practice, however, no such distinction of mono- or dinitrate can be made with certainty and there is no good evidence to suggest that even the primary hydroxyl group is different from the two secondary groups in regard to their relative reactivity with nitric acid. The final product of complete esterification has exactly the composition of the trinitrate ( $C_6H_7O_2(NO_3)_3$ ) and contains 14.15% nitrogen by weight. The commonly used technical means of nitration are insufficient to prepare the 14.15% nitrogen material, in fact, it is not possible to obtain a nitrogen content higher than 13.5% when a mixture of nitric and sulfuric acids is used. However, if phosphoric acid is substituted for sulfuric acid, or if the nitration is carried out in



certain other mixtures, e.g., in a nitric acid-acetic anhydride solution, then the theoretical composition of 14.15% nitrogen can be closely approached.

As the nitrogen content of nitrocellulose decreases from that of the trinitrate (14.15%), there follows a concomitant change in the chemical and physical properties of the polymer. The earlier workers attempted to give a chemical formula to each of the varieties of nitrocellulose with which they were familiar. Such formulations have long been given up, but it is still convenient to retain the terms mono- and di- as well as trinitrate, if only as general indications of the degree of nitration:

Mononitrate ... Nitrogen = 6.76%

Dinitrate ... Nitrogen = 11.12%

Trinitrate ... Nitrogen = 14.15%

Since a nitrocellulose prepared from a mixture of sulfuric and nitric acids is soluble in a particular solvent only when the nitrogen content exceeds about 10.0%, and cannot be made with a nitrogen content higher than 13.5%, then it follows that the useful range of nitrogen contents which can be obtained from this conventional nitrating acid mixture encompasses mainly that of the di- and trinitrate. In fact, the great majority of nitrocelluloses which are useful for industrial purposes have nitrogen contents not very far removed from 12.0%. The more highly nitrated variety containing from 12.9 to 13.5% nitrogen content, which is

made for incorporation into military propellants and explosives, is known by the traditional name of "guncotton". Nitrocelluloses used in propellants contain 12-13.2% nitrogen by weight and consequently, still have a significant number of unnitrated hydroxyl groups randomly distributed along the polymer. These unreacted hydroxyl groups strongly affect the physical and chemical properties of the nitrocellulose polymer. This point is very important and will be discussed again in greater depth in later sections of this report.

#### 1.1.2.2 The Stabilization of Nitrocellulose

Nitrocellulose which has not received the proper stabilizing treatment after nitration is liable to undergo slow spontaneous decomposition which may accelerate into an explosion. The mechanism of this reaction is as follows; the nitrate group oxidizes the cellulose residue and produces nitrous oxides which have an auto-catalytic action. The slow spontaneous decomposition is due to the presence, in very small amounts, of either free mineral acid or certain cellulosic substances formed during the nitration reaction. The reaction becomes more important as the degree of nitration increases but less important when no sulfuric acid is present in the nitrating acid. When these two factors act together, as in the case of a nitrocellulose containing 9-10% of nitrogen prepared with aqueous nitric acid only, mere washing with warm water is usually enough to enable the product to pass all stability tests.

The stabilizing treatment, which is never omitted, takes several forms, but is always essentially one of heating with a large excess of water which, in the first stage of the heating at least, invariably contains a little of the nitrating acid. There are two primary methods of stabilizing nitrocellulose: (1) Steaming or "boiling" at atmospheric pressure and about 100°C which is used for all nitrocelluloses intended for military propellants or blasting explosives. The boiling is generally carried on for several days, with times and changes of water rigidly specified. The later boils are conducted with slightly alkaline water.

(2) Kiering in closed vessels under pressure which is the method applied to the majority of industrial nitrocelluloses. Kiering in closed vessels under pressure serves the dual purpose of stabilization and of viscosity reduction, and is particularly useful when a final product of low viscosity is required. An appreciable amount of nitrogen is lost from the polymer by hydrolysis during both the steaming and kiering processes. After the steaming is completed, all nitrocelluloses intended for propellants and explosives, as well as some industrial varieties are pulped or beaten in paper-beating machines which disintegrate and crush the cotton linter fibers.

## 2. DISCUSSION OF RESULTS

### 2.1 PHYSICAL CHARACTERISTICS OF NITROCELLULOSE-SOLVENT- NO. 2 FUEL OIL MIXTURES

The first series of tests in this project were conducted to determine the physical characteristics of nitrocellulose-solvent and nitrocellulose-solvent-No. 2 fuel oil mixtures. The solubility of smokeless-grade nitrocellulose (Hercules, Grade C, Type 1, 13.15% nitrogen) in candidate solvents identified in a literature search (see item 6.1), No. 2 fuel oil, and toluene was determined. Next, the dilution ratios of nitrocellulose-solvent mixtures were measured, where No. 2 fuel oil was added to the mixture until precipitation occurred. Finally, the viscosities and densities of the nitrocellulose-solvent and nitrocellulose-solvent-No. 2 fuel oil mixtures were determined in this phase of the project. In each section which follows, an introduction will be given to provide the background information required to intelligently discuss the results obtained from each test.

### 2.1.1 Solubility Tests

The so-called lyophilic colloids such as nitrocellulose pass eventually to a state of homogeneous solution in a particular solvent by means of the dual process of gelatinization and swelling. This dual process does not correspond to any process that occurs when a crystalline substance of low or moderate molecular weight forms a homogeneous solution in a solvent. As a consequence, a true solubility limit can not be quantitatively specified for a lyophilic colloid such as nitrocellulose, and it is impossible to have a saturated solution in a single solvent. The radical differences between the physical characteristics of nitrocellulose and a typical crystalline solid arise mainly from the high molecular weight of the nitrocellulose polymer. These differences will now be discussed in greater detail in the following introductory sections.

#### 2.1.1.1 Solubility Behavior of Crystalline Solids

Crystalline solids form homogeneous solutions in a particular solvent by a familiar and well-understood mechanism. The ions or molecules in a crystal of, for example, sodium chloride are in exact array. The distribution of sodium cations and chloride anions throughout the interior of the crystal, neglecting minor irregularities, is quite uniform. On the surface of the crystal there are assemblies of ions or molecules which differ in free energy due to differences between faces of different crystal indices. But the assemblies of higher energy tend to disappear in the presence of a saturated solution, and the crystal as a whole will usually assume a form such that the total energy of the surface layer is a minimum. When dissolution takes place, all the elements at the same energy level are affected at once; all those forming an edge are dissolved together or in rapid succession. There is no half-way stage. Moreover, since the energy differences between an ion on the surface and one in the interior of the crystal are always considerable, there is a very sharp distinction between the two regions; solvent molecules adhere to and eventually detach the outer layer before they are able to reach the internal layers.

#### 2.1.1.2 Solubility Behavior of Nitrocellulose

The interaction of nitrocellulose and a solvent such as acetone is quite different from the situation described for a crystalline solid in the previous section. At no stage is the acetone restricted to the external surface (outer layers) of the nitrocellulose; even when the amount of acetone is relatively small, it is absorbed in the interior and penetrates between the molecular chains which make up the structure of the nitrocellulose polymer, thereby increasing the spacing between them. This phenomenon, termed swelling, takes place at random and is limited by the replacement of the hydroxyl groups along the polymer chain by other groups that endow the polymer with increased solubility. For instance, if the physical conditions of the replacement reaction are uneven, the distribution of subsequent groups may be so irregular that one section of a chain may be soluble (particularly a section in a disorganized region of a chain) while another section (probably in an organized region of a chain where penetration of the solvent has not been as effective) may not have undergone enough replacements to enable it to dissolve; here, the residual hydroxyl groups may be numerous enough to prevent the chains from separating in this region. Only a gelatinous mass, which still possesses a regular structure, results at this point in the addition of the acetone. With the addition of a greater amount of acetone, the molecular array becomes confused, the chain alignment is lost, and a gelatinous mass of no regular structure results. Finally, when an excess of solvent has been added, the polymer chains become completely separated and a true solution forms.<sup>7</sup>

There is one general rule to consider when compiling a list of candidate solvents for nitrocellulose--no substance is a solvent unless its molecule contains a polar group. Acetone, which contains a polar carbonyl oxygen (C=O) group, has been shown to be the most effective solvent for nitrocelluloses of various nitrogen contents. In fact, the aliphatic ketones and the esters of the saturated fatty acids are probably the only two classes of solvents which contain at least some members that can be relied on to dissolve all nitrocelluloses of any nitrogen content (exceeding 10.5%) and of any viscosity. However, the activity of the ketones and esters has been found to decrease as the length of the hydrocarbon chain increases.

Alcohols have a limited solvent power for nitrocellulose, while glycerine has none. No nitrocellulose dissolves to a quite clear solution in pure ethyl alcohol unless the nitrocellulose has a nitrogen content of from 10.6 to 11.0% and a low viscosity. Swelling or solution is incomplete at ambient temperature in pure ethyl alcohol with nitrocelluloses having a nitrogen content greater than 11.0%. Methyl alcohol, although for solvent power is as much dependent on the degree of nitration of the nitrocellulose as ethyl alcohol, is nevertheless much more complete in its action and will dissolve entirely many nitrocelluloses containing 12.6% nitrogen or less.

Nitrocompounds of either the aliphatic or aromatic series, especially the latter, have considerable application in the production of



nitrocellulose-containing lacquers. Aliphatic nitrates, anilides, substituted ureas, urethanes, cyanides, isocyanates and many heterocyclic alcohols and ketones such as furfural and camphor also possess some solvent power for nitrocellulose. Amines could be used to solubilize nitrocellulose, unfortunately, they also cause decomposition. Glacial acetic acid is a solvent for nitrocellulose, while fatty acids with long chains are not.

Composite solvents, made up of at least one true solvent with one or more diluents of feeble solvent power are in practice very important, because diluents are usually relatively inexpensive and the objective is always to use as much of them as possible. A composite solvent is usually a better solvent for a particular nitrocellulose than either component solvent by itself. In most cases, the limiting factor in how much diluent can be added to form a particular composite solvent is its precipitating power, i.e., how much diluent can be tolerated before the nitrocellulose precipitates from solution. Unfortunately, the common paraffin hydrocarbons (such as No. 2 fuel oil) possess the greatest precipitating power for nitrocellulose since they are the only substances practically devoid of any polar groups within their molecular structure. As such, the common paraffin hydrocarbons can be used only in limited amounts as diluents in a composite solvent for nitrocellulose. In practice, ethyl and butyl alcohol, benzene, toluene and xylene are preferable to paraffin hydrocarbons as diluents. The number of composite solvents actually used, particularly for the preparation of various

lacquer formulations containing nitrocellulose, is quite high and a complete cataloging of them in this discussion would have little point.

Finally, as mentioned previously, when certain solvents and composite solvent systems are used, the percent nitrogen content of the nitrocellulose determines the amount of polymer that is soluble. For example, nitrocellulose having a nitrogen content of 10 to 12.6% is soluble in a 2:1 ratio ether/ethanol solvent system, whereas nitrocellulose having a nitrogen content of greater than 13% or less than 10% is not soluble.

#### 2.1.1.3 Solubility Results from Smokeless-Grade Nitrocellulose

Based on the information presented in the above discussion, as well as additional information compiled from a literature search, five potential solvents for the smokeless-grade (13.15% nitrogen) nitrocellulose were selected for use in the solubility tests. These five solvents were acetone, 2-butanone, tetrahydrofuran, ethyl acetate, and butyl acetate. In addition, the solubility of nitrocellulose in toluene and No. 2 fuel oil was evaluated.

The procedure for conducting the solubility tests is given in section 4.4.1. Each solubility test was conducted at 25°C. The maximum concentration of nitrocellulose in each solvent which could be attained in each test was limited by the ability of the solubility apparatus to

adequately stir the nitrocellulose-solvent solution. For example, the maximum concentration of nitrocellulose in acetone investigated in the solubility test was 7.5% by weight. Above this concentration, the nitrocellulose-acetone solution became a viscous gel and the experiment had to be terminated.

In fact, for each of the other four solvents investigated in the solubility tests, a situation similar to that with the nitrocellulose-acetone solutions was encountered. The only difference was the maximum concentration of nitrocellulose attained in each solvent before a viscous gel occurred. For 2-butanone, the maximum concentration of nitrocellulose investigated was 6.6% by weight; for tetrahydrofuran, 6.6% by weight; for ethyl acetate, 4.8% by weight; and finally, for butyl acetate, 4.4% by weight.

It is important to note that these maximum concentrations of nitrocellulose attained in each solvent before the mixture became a viscous gel provided important information required before the dilution ratio tests, described in the next section, were attempted. This information was, in fact, more important for the successful completion of this project than was the definition of actual solubility limits, which as mentioned earlier is not a practical concept to invoke when discussing solutions containing nitrocellulose.

Finally, the smokeless-grade nitrocellulose was found to be insoluble in both toluene and No. 2 fuel oil at temperatures of 25, 40, and 55°C. The solubility "value" in each case was less than 0.010 g/ml. These results are not surprising based on the fact that paraffin hydrocarbons are known to be powerful diluents for nitrocellulose solutions. The solubility of nitrocellulose in toluene was evaluated at the request of USATHAMA personnel, since toluene is currently being used as a solvent in another project to develop a process for burning fuel oil containing explosives as a supplemental fuel for use in Army industrial combustors.

#### 2.1.2 Dilution Ratio Tests

##### 2.1.2.1 Introduction

The dilution ratio method, which involves the determination of the volume of diluent liquid required to just cause precipitation of a cellulosic material from solution, is often used as a means of assessing the solvent power of solvents for high polymers, especially cellulose derivatives. The dilution ratio method also yields important technical information regarding the ability of solutions to tolerate additions of diluent liquids. The dilution ratio is defined as the total volume of diluent added to the system divided by the total volume of solvent present. In the tests described below, the diluent liquid used was, of course, No. 2 fuel oil. The five solvents investigated were acetone, tetrahydrofuran, ethyl acetate, butyl acetate, and 2-butanone.

#### 2.1.2.2 Results and Discussion

The results from the dilution ratio tests with each solvent are summarized in Table 1. The maximum concentration of nitrocellulose in each solvent was dictated by the fact that the nitrocellulose-solvent solution had to be able to be swirled by hand in order to carry out the dilution ratio test according to American Society for Testing Materials (ASTM) D1720-88 standard procedure. Guideline maximum concentrations of nitrocellulose in each solvent were previously established in the solubility tests. In fact, the maximum concentrations of nitrocellulose in each solvent investigated in these dilution ratio tests were slightly lower than those used in the solubility tests.

Solutions of nitrocellulose in butyl acetate (Figure 3) were able to tolerate the greatest additions of No. 2 fuel oil before precipitation occurred. Unfortunately, the maximum concentration of nitrocellulose which could be attained in the butyl acetate before it became impossible to swirl the mixture in the flask and adequately perform the dilution ratio tests was only 4.1%, the lowest concentration of the five solvents investigated.

Higher concentrations of nitrocellulose in ethyl acetate (5.3%), tetrahydrofuran (5.4%), and 2-butanone (5.9%) could be attained before it became impossible to swirl the mixtures in the flask than was the case for butyl acetate. However, the dilution ratios for various

concentrations of nitrocellulose in ethyl acetate (Figure 4), tetrahydrofuran (Figure 5), and 2-butanone (Figure 6) were each lower, respectively, than the dilution ratios found for the nitrocellulose-butyl acetate mixtures.

Finally, the highest concentration of nitrocellulose in acetone (8.3%) could be attained before it became impossible to swirl the mixture in the flask and effectively perform the dilution ratio experiment. Unfortunately, solutions of nitrocellulose in acetone were the least able to tolerate additions of the No. 2 fuel oil diluent (Figure 7). More importantly, when the nitrocellulose did precipitate from solution, it formed a gelatinous mass which was difficult to redisperse in solution and which tended to coat the sides of the flask with a thick gummy film. This result highlighted a potentially serious problem which could arise if the nitrocellulose-acetone mixture was mixed with a tank of No. 2 fuel oil prior to being fed to a burner. Specifically, if too much No. 2 fuel oil was inadvertently added to the nitrocellulose-acetone mixture, thereby exceeding the dilution ratio for a particular nitrocellulose-acetone solution, then precipitation of the nitrocellulose would occur which could potentially block fuel lines or clog a burner. Such an occurrence would obviously be unacceptable.

Table 1. Summary of Results from Dilution Ratio Experiments<sup>a</sup> for Solvent-Nitrocellulose (NC) Mixtures

| <u>Solvent<sup>b</sup></u> | <u>Initial<br/>Wt. %<br/>NC</u> | <u>First<br/>Endpoint(ml)</u> | <u>Total<br/>Solvent(ml)</u> | <u>Second<br/>Endpoint(ml)</u> | <u>Dilution<br/>Ratio</u> |
|----------------------------|---------------------------------|-------------------------------|------------------------------|--------------------------------|---------------------------|
| Acetone                    | 1.4                             | 26.5                          | 52.0                         | 27.0                           | 0.519                     |
|                            | 3.7                             | 23.5                          | 51.0                         | 24.0                           | 0.471                     |
|                            | 6.0                             | 22.0                          | 51.0                         | 22.6                           | 0.443                     |
|                            | 8.3                             | 20.0                          | 52.0                         | 21.5                           | 0.414                     |
| Ethyl<br>Acetate           | 1.2                             | 62.0                          | 53.0                         | 71.0                           | 1.340                     |
|                            | 3.3                             | 48.0                          | 52.0                         | 51.2                           | 0.985                     |
|                            | 5.3                             | 42.0                          | 53.0                         | 44.0                           | 0.830                     |
|                            | 7.3 <sup>c</sup>                | --                            | --                           | --                             | --                        |
| THF <sup>d</sup>           | 1.2                             | 49.0                          | 52.0                         | 50.7                           | 0.975                     |
|                            | 3.3                             | 46.0                          | 53.0                         | 47.5                           | 0.896                     |
|                            | 5.4                             | 43.0                          | 52.0                         | 45.0                           | 0.865                     |
|                            | 7.3 <sup>c</sup>                | --                            | --                           | --                             | --                        |
| 2-Butanone                 | 1.4                             | 47.0                          | 52.0                         | 48.0                           | 0.923                     |
|                            | 3.7                             | 38.0                          | 53.0                         | 44.0                           | 0.830                     |
|                            | 5.9                             | 39.0                          | 53.0                         | 43.0                           | 0.811                     |
|                            | 7.0 <sup>c</sup>                | --                            | --                           | --                             | --                        |
| Butyl<br>Acetate           | 1.4                             | 92.0                          | 53.0                         | 95.0                           | 1.792                     |
|                            | 2.8                             | 76.0                          | 52.0                         | 85.0                           | 1.635                     |
|                            | 4.1                             | 56.0                          | 53.0                         | 62.0                           | 1.170                     |
|                            | 5.4 <sup>c</sup>                | --                            | --                           | --                             | --                        |

<sup>a</sup>Dilution Ratios determined similar to ASTM D1720-88 with No. 2 fuel oil as the diluent.

<sup>b</sup>Initial volume of solvent in each experiment was 50 ml.

<sup>c</sup>Mixture too viscous to swirl and effectively perform the Dilution Ratio experiment.

<sup>d</sup>THF = tetrahydrofuran.

Dilution Ratios of NC/BuAc Solutions  
(ASTM D 1720-88)

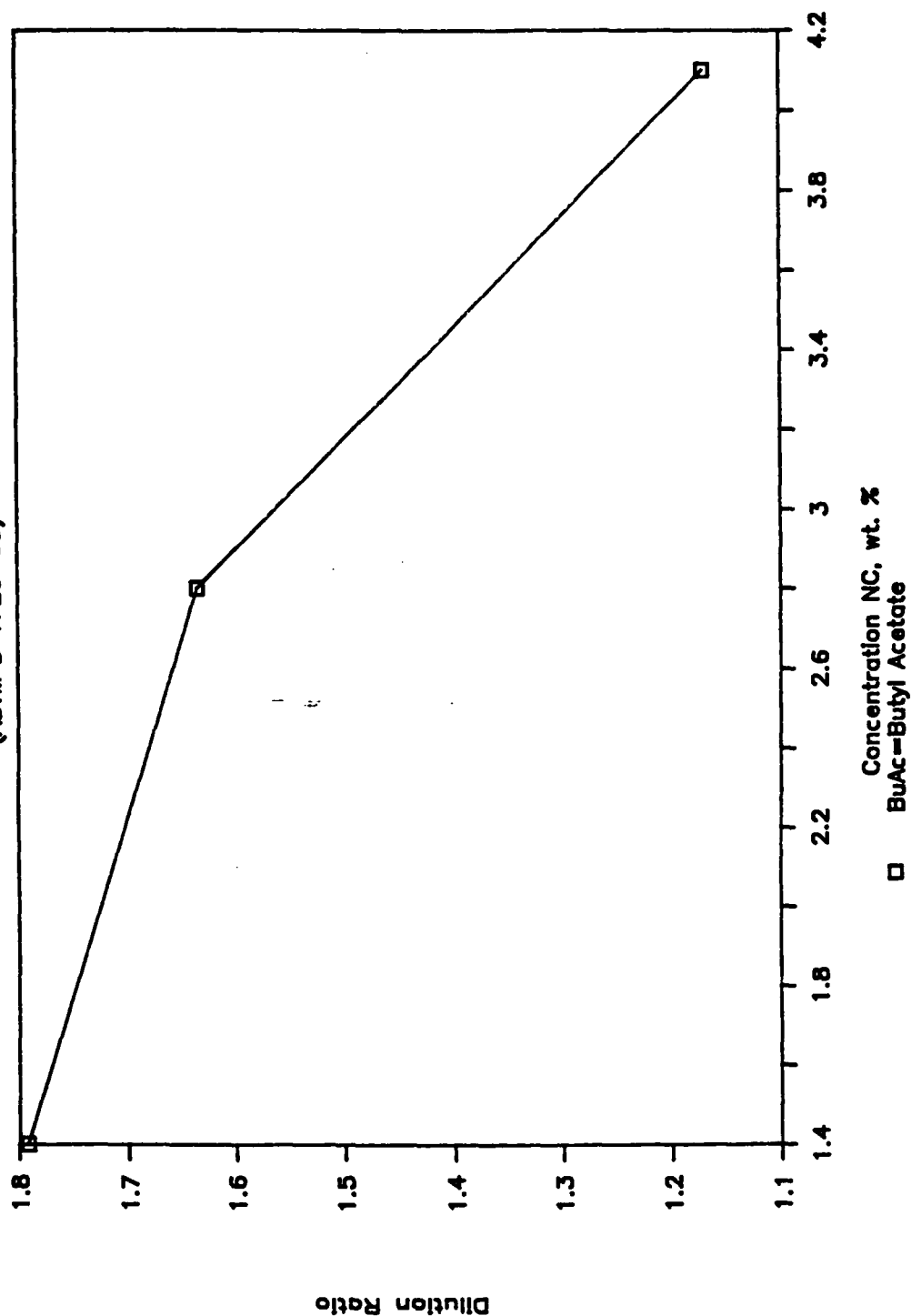


Figure 3. Results from Dilution Ratio Tests for Nitrocellulose (NC)-Butyl Acetate Solutions.



# Dilution Ratios of NC/EtAc Solutions (ASTM D 1720-88)

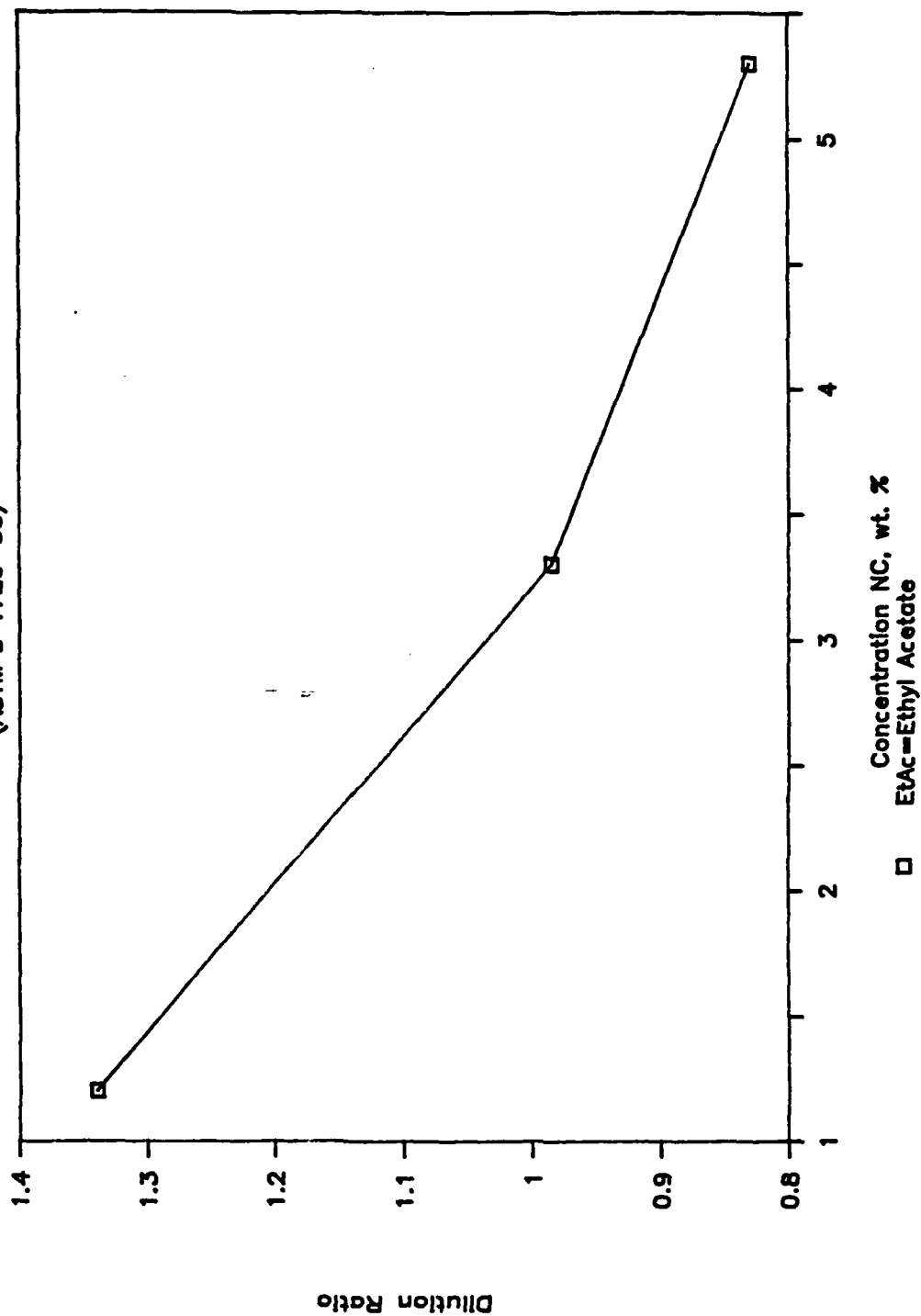


Figure 4. Results from Dilution Ratio Tests for Nitrocellulose (NC)-Ethyl Acetate Solutions.

# Dilution Ratios of NC/THF Solutions (ASTM D 1720-88)

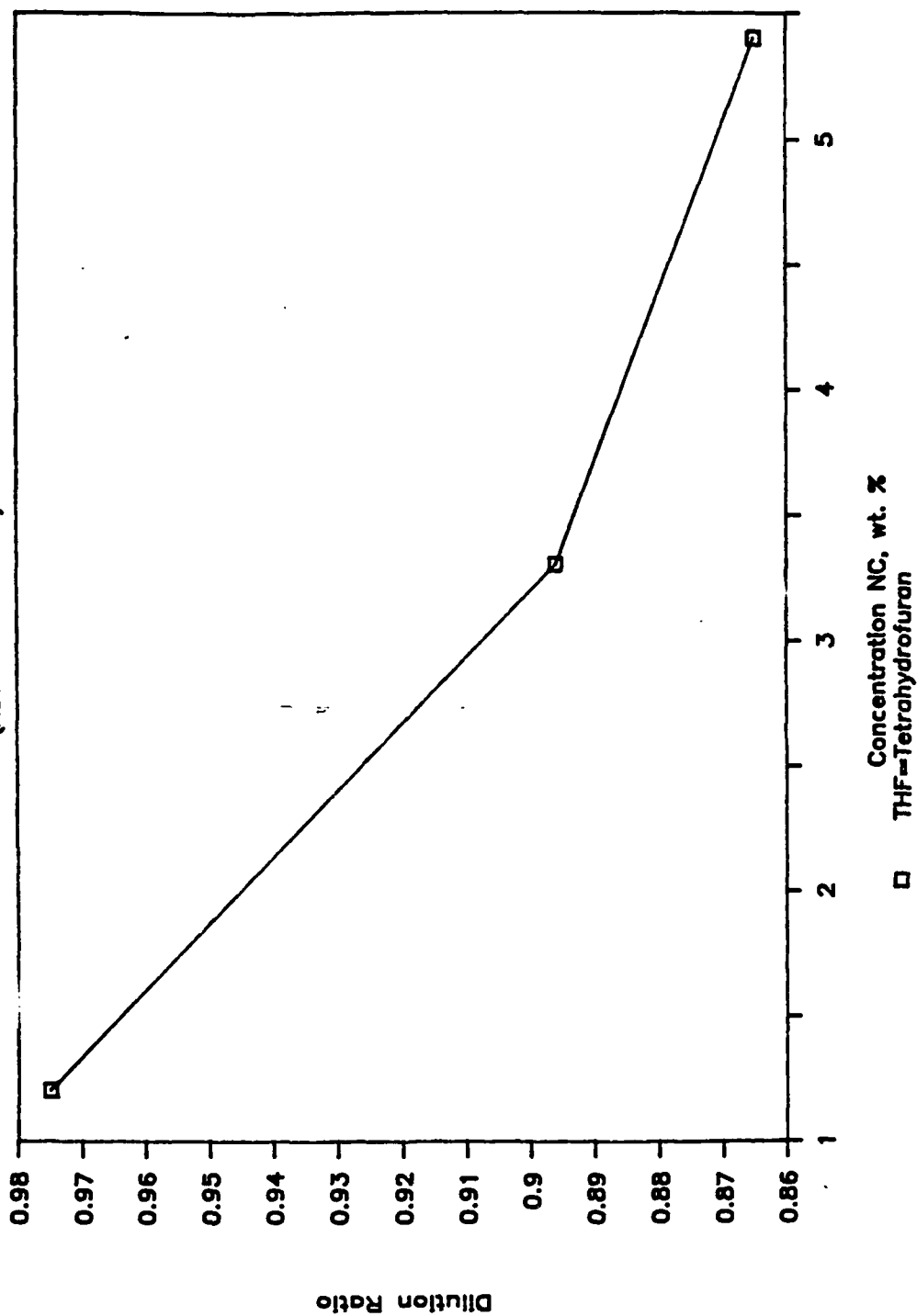


Figure 5. Results from Dilution Ratio Tests for Nitrocellulose (NC)-Tetrahydrofuran Solutions.

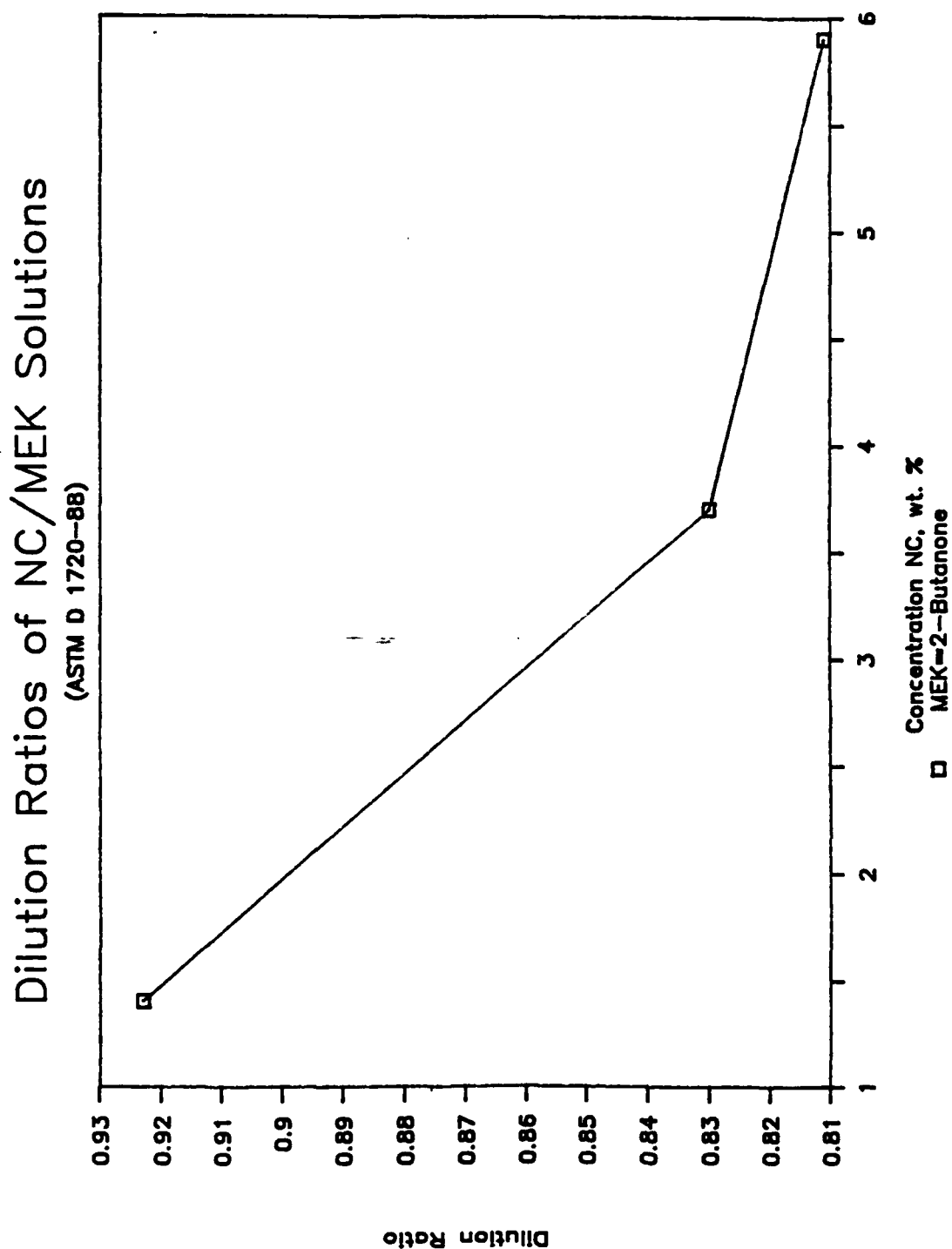


Figure 6. Results from Dilution Ratio Tests for Nitrocellulose (NC)-2-Butanone Solutions.

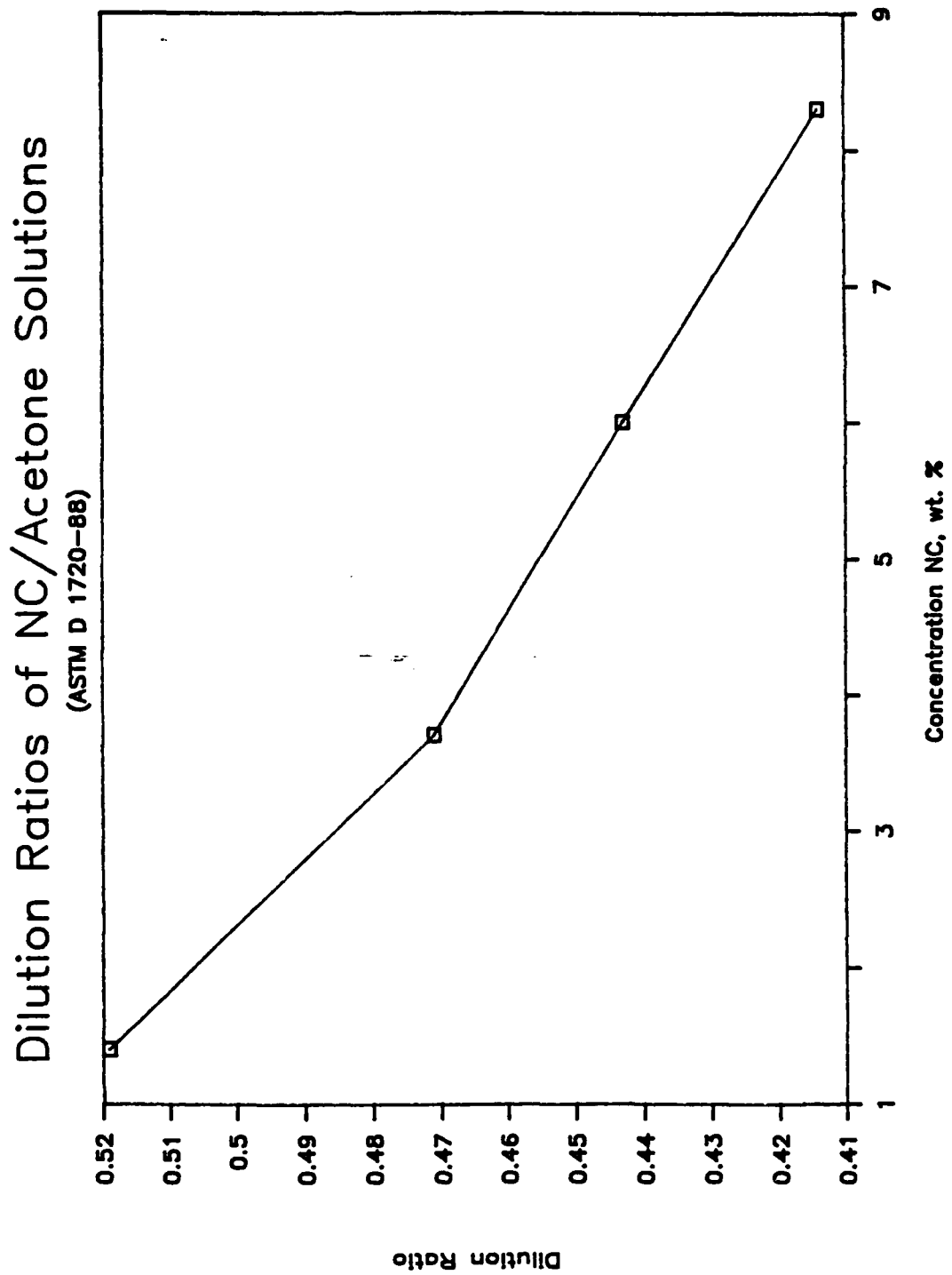


Figure 7. Results from Dilution Ratio Tests for Nitrocellulose (NC)-Acetone Solutions.

### 2.1.3 Density Tests

The densities of various nitrocellulose-solvent and nitrocellulose-solvent-No. 2 fuel oil mixtures were measured at 20 and 50°C using glass hydrometers according to ASTM D1298-85 standard procedure. The results obtained at 20 and 50°C for each type of mixture are summarized in Table 2 and Table 3, respectively. The densities of these mixtures are relatively unremarkable; in fact, the main reason that the densities of each nitrocellulose-solvent and nitrocellulose-solvent-No. 2 fuel oil solution was measured was to provide the data required for calculating the viscosity of each mixture. The viscosity data is more informative and will be discussed in the following section.

### 2.1.4 Viscosity Tests

#### 2.1.4.1 Introduction

Very dilute solutions of nitrocellulose (i.e., less than 0.05% nitrocellulose) are low viscosity mixtures which exhibit typical Newtonian behavior in that the rate of flow is proportional to the applied stress or pressure. On the other hand, even only slightly concentrated solutions of nitrocellulose (i.e., greater than 0.5% nitrocellulose) will develop a high viscosity and exhibit non-Newtonian behavior.

Table 2. Densities of Nitrocellulose (NC)-Solvent Mixtures  
at 20 and 50°C

| <u>Solvent</u>   | <u>Wt. % NC</u> | <u>Density (g/ml, 20°C)</u> | <u>Density (g/ml, 50°C)</u> |
|------------------|-----------------|-----------------------------|-----------------------------|
| Acetone          | 0.0             | 0.780                       | 0.739                       |
|                  | 1.0             | 0.784                       | 0.744                       |
|                  | 2.1             | 0.790                       | 0.748                       |
|                  | 3.9             | 0.799                       | 0.758                       |
|                  | 5.8             | 0.809                       | 0.769                       |
|                  | 7.5             | 0.826                       | 0.782                       |
| Ethyl<br>Acetate | 0.0             | 0.887                       | 0.844                       |
|                  | 1.0             | 0.903                       | 0.853                       |
|                  | 2.0             | 0.908                       | 0.855                       |
|                  | 3.1             | 0.911                       | 0.856                       |
|                  | 4.0             | 0.914                       | 0.860                       |
|                  | 4.8             | 0.929                       | 0.864                       |
| THF              | 0.0             | 0.886                       | ND <sup>a</sup>             |
|                  | 1.0             | 0.892                       | ND <sup>a</sup>             |
|                  | 2.4             | 0.899                       | ND <sup>a</sup>             |
|                  | 3.9             | 0.907                       | ND <sup>a</sup>             |
|                  | 5.3             | 0.916                       | ND <sup>a</sup>             |
|                  | 6.6             | 0.927                       | ND <sup>a</sup>             |
| 2-Butanone       | 0.0             | 0.799                       | ND <sup>a</sup>             |
|                  | 1.0             | 0.798                       | ND <sup>a</sup>             |
|                  | 2.5             | 0.813                       | ND <sup>a</sup>             |
|                  | 4.0             | 0.816                       | ND <sup>a</sup>             |
|                  | 5.3             | 0.827                       | ND <sup>a</sup>             |
|                  | 6.6             | 0.832                       | ND <sup>a</sup>             |
| Butyl<br>Acetate | 0.0             | 0.879                       | 0.833                       |
|                  | 0.5             | 0.883                       | 0.837                       |
|                  | 1.6             | 0.886                       | 0.839                       |
|                  | 2.5             | 0.888                       | 0.843                       |
|                  | 3.5             | 0.894                       | 0.848                       |
|                  | 4.4             | 0.902                       | 0.854                       |

<sup>a</sup>ND = Not determined. Tetrahydrofuran (THF) and 2-Butanone  
previously eliminated from further testing based on cost  
and health analysis data.

Table 3. Densities of Nitrocellulose (NC)-Solvent-No. 2 Fuel Oil Mixtures at 20 and 50°C.

| <u>Solvent</u>   | <u>Wt. %<br/>Solvent</u> | <u>Wt. %<br/>NC</u> | <u>Wt. %<br/>Fuel Oil</u> | <u>Density (g/ml)<br/>(at 20°C)</u> | <u>Density (g/ml)<br/>(at 50°C)</u> |
|------------------|--------------------------|---------------------|---------------------------|-------------------------------------|-------------------------------------|
| Fuel Oil         | 0.0                      | 0.0                 | 100.0                     | 0.851                               | 0.826                               |
| Acetone          | 100.0                    | 0.0                 | 0.0                       | 0.780                               | 0.739                               |
|                  | 65.7                     | 0.7                 | 33.6                      | 0.794                               | 0.773                               |
|                  | 66.5                     | 1.4                 | 32.1                      | 0.801                               | 0.774                               |
|                  | 66.4                     | 2.7                 | 30.9                      | 0.806                               | 0.780                               |
|                  | 66.3                     | 4.1                 | 29.6                      | 0.814                               | 0.785                               |
|                  | 68.5                     | 5.6                 | 25.9                      | ND <sup>a</sup>                     | ND <sup>a</sup>                     |
| Ethyl<br>Acetate | 100.0                    | 0.0                 | 0.0                       | 0.887                               | 0.844                               |
|                  | 56.5                     | 0.6                 | 42.9                      | 0.860                               | 0.834                               |
|                  | 58.6                     | 1.2                 | 40.2                      | 0.862                               | 0.840                               |
|                  | 56.5                     | 1.8                 | 41.7                      | 0.867                               | 0.845                               |
|                  | 58.1                     | 2.4                 | 39.5                      | 0.865                               | 0.844                               |
|                  | 61.4                     | 3.1                 | 35.5                      | ND <sup>a</sup>                     | ND <sup>a</sup>                     |
| Butyl<br>Acetate | 100.0                    | 0.0                 | 0.0                       | 0.879                               | 0.833                               |
|                  | 39.0                     | 0.2                 | 60.8                      | 0.851                               | 0.826                               |
|                  | 38.9                     | 0.7                 | 60.4                      | 0.852                               | 0.831                               |
|                  | 40.3                     | 1.0                 | 58.7                      | 0.850                               | 0.829                               |
|                  | 44.4                     | 1.6                 | 54.0                      | ND <sup>a</sup>                     | 0.849                               |
|                  | 49.1                     | 2.3                 | 48.6                      | ND <sup>a</sup>                     | ND <sup>a</sup>                     |

<sup>a</sup>ND = Not determined. Mixture too thick and viscous to introduce into the viscometer.

Nitrocellulose has been the polymeric material of choice for innumerable investigations of the viscosity of lyophilic colloid solutions. Two classic reviews of an immense volume of work were published in 1926 by McBain and his collaborators<sup>8,9</sup> before the present theories regarding viscosity or rheology had developed. McBain et al. used a nitrocellulose containing 12.1% nitrogen by weight throughout all of their investigations. The viscosities of solutions of this particular nitrocellulose at concentrations of 0.3-0.5% in a long list of solvents of every possible type were measured. These researchers demonstrated that the viscosity depended on the solvent, and the conclusion of their studies was that the best solvents (i.e., those with the greatest solvent power) yielded the least viscous solutions.

This concept of solvent power has been widely accepted, especially in technical work with nitrocellulose-containing lacquers where the amount of nitrocellulose which can be dissolved in a solvent system without the troublesome physical characteristics of high viscosity developing is the most important consideration. As one example, acetone solutions containing only 4% by weight nitrocellulose are quite viscous, while if a more viscous solvent such as amyl acetate is used, the system frequently becomes a transparent gel at this concentration. Thus, acetone is a better solvent for nitrocellulose than amyl acetate. This concept of solvent power will be used during the remainder of the discussion in this section.



As stated above, McBain et al. found that the viscosities of nitrocellulose solutions strongly depend on the relative chemical nature of the solvent and solute. This observation is nicely illustrated by variations in the chemical composition of the nitrocellulose as nitric groups replace hydroxyl groups, thereby increasing the nitrogen content of the resulting polymer. These researchers found a wider range of solvents for the nitrocellulose of 10.5% nitrogen content compared with the range of solvents which could dissolve another nitrocellulose of 12.2% nitrogen content. For example, the nitrocellulose with a high nitrogen content was insoluble in some ether-alcohol-water mixtures. With the nitrocellulose of lower nitrogen content, the range of such solvent mixtures which dissolved the nitrocellulose increased.

This variation of the viscosity of nitrocellulose solutions with the concentration of the nitrocellulose solute is a quite general attribute of colloid solutions. Another general attribute of colloid solutions is that temperature changes result in alterations of the viscosity of the solutions, however, no simple mathematical equation between the temperature and the viscosity of the nitrocellulose solution has been proposed in the literature.

#### 2.1.4.2 Falling Ball Viscometer

To obtain atomization in an oil burner, it has been determined that the viscosity of the oil should not exceed a range of 20 to 30 centistokes at the burner tip<sup>3</sup>. At temperatures of 20 and 50°C, the neat No. 2 fuel oil exhibited viscosities of 5.3 and 2.5 centistokes, respectively.

The viscosities of various nitrocellulose-solvent and nitrocellulose-solvent-No. 2 fuel oil solutions measured at 20 and 50°C with the falling ball viscometer according to ASTM D1343-86 standard procedure are summarized in Table 4 and Table 5, respectively. Only the viscosity data obtained from the solutions of nitrocellulose in acetone, ethyl acetate, and butyl acetate solutions will be discussed here; although data obtained at 20°C are presented in Table 4 for nitrocellulose-tetrahydrofuran and nitrocellulose-2-butanone solutions, the viscosities of these solutions were not obtained at 50°C, and No. 2 fuel oil was not added to these solutions, thereby accounting for the lack of viscosity data in Table 5, because tetrahydrofuran and 2-butanone were previously eliminated from further testing based on cost and health analysis data. Tetrahydrofuran and 2-butanone were eliminated from further testing by mutual agreement between USATHAMA and TVA.

Table 4. Viscosities of Nitrocellulose (NC)-Solvent Mixtures at 20 and 50°C.

| <u>Solvent</u>   | <u>Wt. %<br/>NC</u> | <u>Viscosity<sup>a</sup><br/>(centistokes)</u> | <u>Viscosity<sup>b</sup><br/>(centistokes)</u> |
|------------------|---------------------|--|--|
| Acetone          | 0.0                 | 0.454  | 0.358  |
|                  | 1.0                 | 3.7  | 2.1  |
|                  | 2.1                 | 18.7   | 8.0  |
|                  | 3.9                 | 125.2  | 55.2   |
|                  | 5.8                 | 534.6  | 196.2  |
|                  | 7.5                 | 1723.9   | 595.8  |
| Ethyl<br>Acetate | 0.0                 | 0.547  | 0.409  |
|                  | 1.0                 | 10.0   | 3.7  |
|                  | 2.0                 | 68.2   | 20.2   |
|                  | 3.1                 | 210.9  | 85.8   |
|                  | 4.0                 | 654.4  | 228.5  |
|                  | 4.8                 | 1702.9   | 468.4  |
| THF <sup>c</sup> | 0.0                 | 0.588  | 0.465  |
|                  | 1.0                 | 9.9  | 4.7  |
|                  | 2.4                 | 116.1  | ND <sup>d</sup>                                |
|                  | 3.9                 | 455.3  | ND <sup>d</sup>                                |
|                  | 5.3                 | 1641.9   | ND <sup>d</sup>                                |
|                  | 6.6                 | 3311.8   | ND <sup>d</sup>                                |
| 2-Butanone       | 0.0                 | 0.501  | 0.369  |
|                  | 1.0                 | 5.4  | ND <sup>d</sup>                                |
|                  | 2.5                 | 54.0   | ND <sup>d</sup>                                |
|                  | 4.0                 | 207.0  | ND <sup>d</sup>                                |
|                  | 5.3                 | 728.9  | ND <sup>d</sup>                                |
|                  | 6.6                 | 3257.2   | ND <sup>d</sup>                                |
| Butyl<br>Acetate | 0.0                 | 0.878  | 0.598  |
|                  | 0.5                 | 4.0  | 1.7  |
|                  | 1.6                 | 54.1   | 15.5   |
|                  | 2.5                 | 172.3  | 59.7   |
|                  | 3.5                 | 743.2  | 218.0  |
|                  | 4.4                 | 2141.8   | 544.3  |

<sup>a</sup>At 20°C.

<sup>b</sup>At 50°C.

<sup>c</sup>THF = Tetrahydrofuran.

<sup>d</sup>ND = Not determined. THF and 2-Butanone previously eliminated from further testing based on cost and health analysis data.

Table 5. Viscosities of Nitrocellulose (NC)-Solvent-No. 2 Fuel Oil Mixtures at 20 and 50°C.

| <u>Solvent</u>   | <u>Wt. %<br/>Solvent</u> | <u>Wt. %<br/>NC</u> | <u>Wt. %<br/>Fuel Oil</u> | <u>Viscosity<sup>a</sup><br/>(centistokes)</u> | <u>Viscosity<sup>b</sup><br/>(centistokes)</u> |
|------------------|--------------------------|---------------------|---------------------------|--|--|
| Fuel Oil         | 0.0                      | 0.0                 | 100.0                     | 5.3  | 2.5  |
| Acetone          | 100.0                    | 0.0                 | 0.0                       | 0.454  | 0.358  |
|                  | 65.7                     | 0.7                 | 33.6                      | 4.6  | 2.5  |
|                  | 66.5                     | 1.4                 | 32.1                      | 24.5   | 8.9  |
|                  | 66.4                     | 2.7                 | 30.9                      | 169.5  | 73.3   |
|                  | 66.3                     | 4.1                 | 29.6                      | 1140.8   | 270.2  |
|                  | 68.5                     | 5.6                 | 25.9                      | ND <sup>c</sup>                                | ND <sup>c</sup>                                |
| Ethyl<br>Acetate | 100.0                    | 0.0                 | 0.0                       | 0.547  | 0.409  |
|                  | 56.5                     | 0.6                 | 42.9                      | 4.9  | 2.5  |
|                  | 58.6                     | 1.2                 | 40.2                      | 50.6   | 14.6   |
|                  | 56.5                     | 1.8                 | 41.7                      | 67.4   | 45.3   |
|                  | 58.1                     | 2.4                 | 39.5                      | 1978.0   | 243.1  |
|                  | 61.4                     | 3.1                 | 35.5                      | ND <sup>c</sup>                                | ND <sup>c</sup>                                |
| Butyl<br>Acetate | 100.0                    | 0.0                 | 0.0                       | 0.878  | 0.598  |
|                  | 39.0                     | 0.2                 | 60.8                      | 5.3  | 2.5  |
|                  | 38.9                     | 0.7                 | 60.4                      | 5.9  | 1.8  |
|                  | 40.3                     | 1.0                 | 58.7                      | 10.4   | 1.9  |
|                  | 44.4                     | 1.6                 | 54.0                      | ND <sup>c</sup>                                | 437.5  |
|                  | 49.1                     | 2.3                 | 48.6                      | ND <sup>c</sup>                                | ND <sup>c</sup>                                |

<sup>a</sup>At 20°C.

<sup>b</sup>At 50°C.

<sup>c</sup>ND = Not determined. Mixture too thick and viscous to introduce into the viscometer.

The viscosities of nitrocellulose-acetone solutions increase rapidly at both 20 and 50°C as the nitrocellulose concentration increases from 1.0 to 7.5 weight percent (Figure 8). At this point, let us assume for a moment that the objective of this project was to burn a mixture of nitrocellulose and acetone only (of course, this would be tremendously expensive). At a concentration of approximately 2.4% by weight nitrocellulose in acetone at 20°C, the viscosity of this solution will exceed the 30 centistoke upper limit to obtain atomization in an oil burner. Similarly, at a slightly higher concentration of approximately 3.1% by weight nitrocellulose in acetone at 50°C, the viscosity of this solution will again exceed the 30 centistoke upper limit for use as a fuel to fire a conventional oil burner. These concentrations are rather low when one considers the large amount of waste and out-of-specification propellant in the military's inventory currently awaiting disposal.

The situation does not improve when No. 2 fuel oil is blended with the nitrocellulose-acetone solutions. Again, the viscosities of the nitrocellulose-acetone-No. 2 fuel oil solutions increase rapidly at 20 and

# Viscosities of NC/Acetone Solutions

(ASTM D 1343-86)

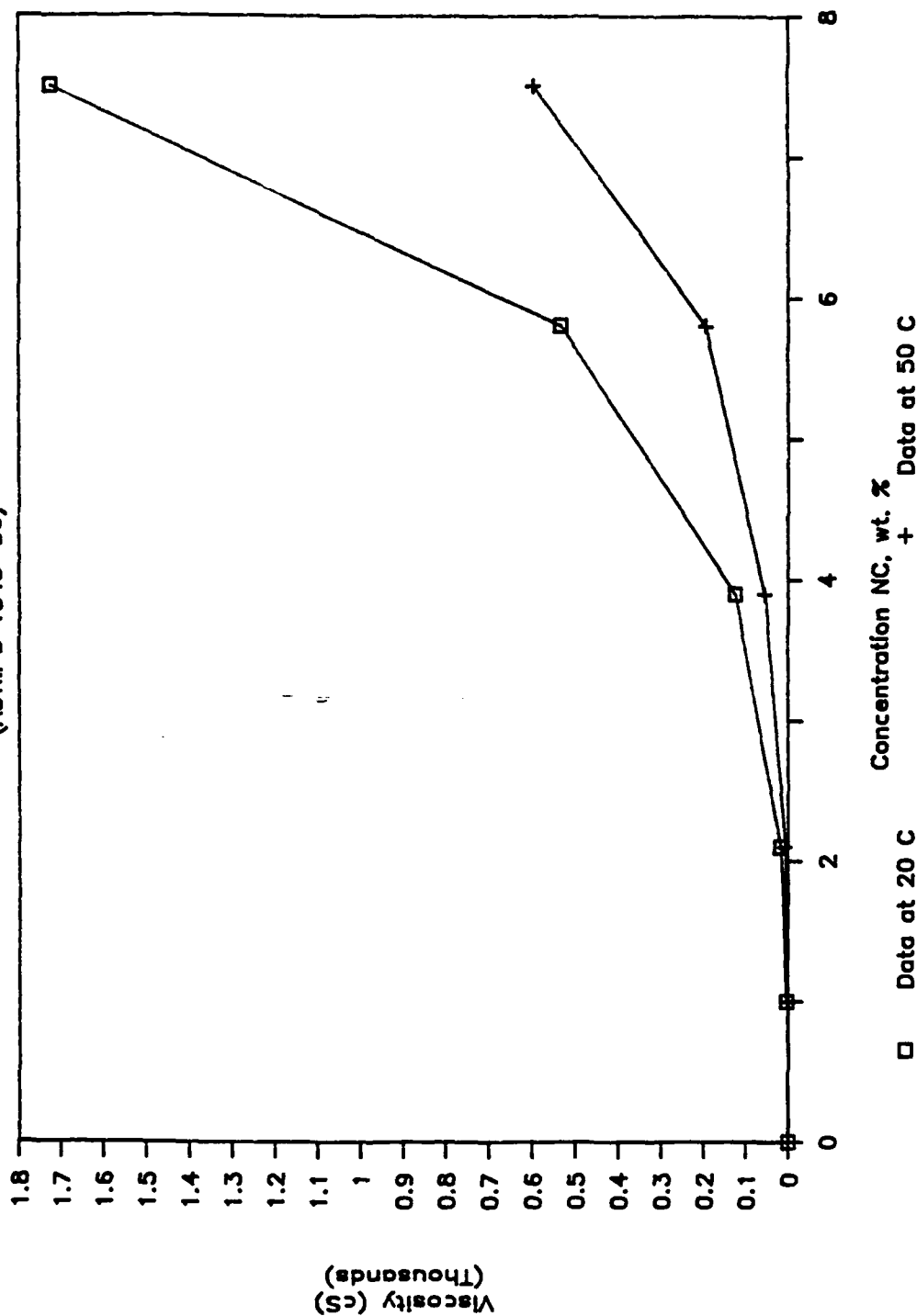


Figure 8. The Viscosities of Nitrocellulose (NC)-Acetone Solutions at 20 and 50°C.

50°C as the nitrocellulose concentration increases from 0.7 to 4.1 weight percent (Figure 9). In reality, of course, the objective of this project was to perform a technical and economic evaluation of the concept of burning a mixture of nitrocellulose and solvent (acetone) blended with No. 2 fuel oil. At a nitrocellulose concentration of approximately 1.5 weight percent in the acetone-No. 2 fuel oil mixture (66.5% acetone, 32.1% fuel oil), the viscosity of this solution will exceed the 30 centistoke upper limit to obtain atomization in an oil burner. Similarly, at a slightly higher nitrocellulose concentration of approximately 1.8% by weight in the same acetone-No. 2 fuel oil mixture described above, the viscosity of this solution will exceed the 30 centistoke upper limit for use as a fuel to fire a conventional oil burner. A temperature of 50-55°C for a feed solution to an oil burner is a reasonable value.

Therefore, the conclusion of this analysis of the viscosity data for nitrocellulose-acetone-No. 2 fuel oil mixtures is that a maximum concentration of approximately 2% by weight nitrocellulose in the acetone-No. 2 fuel oil solution could be burned in a typical atomizing oil burner. As will be clearly demonstrated in the economic analysis (section 3.2), burning a 2% by weight solution of nitrocellulose in acetone-No. 2 fuel oil would not only take an unacceptably long time to dispose of the large amount of waste and out-of-specification propellants in the military's inventory, but would also be prohibitably expensive.

# Viscosity of NC/Acetone/Fuel Oil Soln's

(Acetone, 66-67%; Fuel Oil, 30-34%)

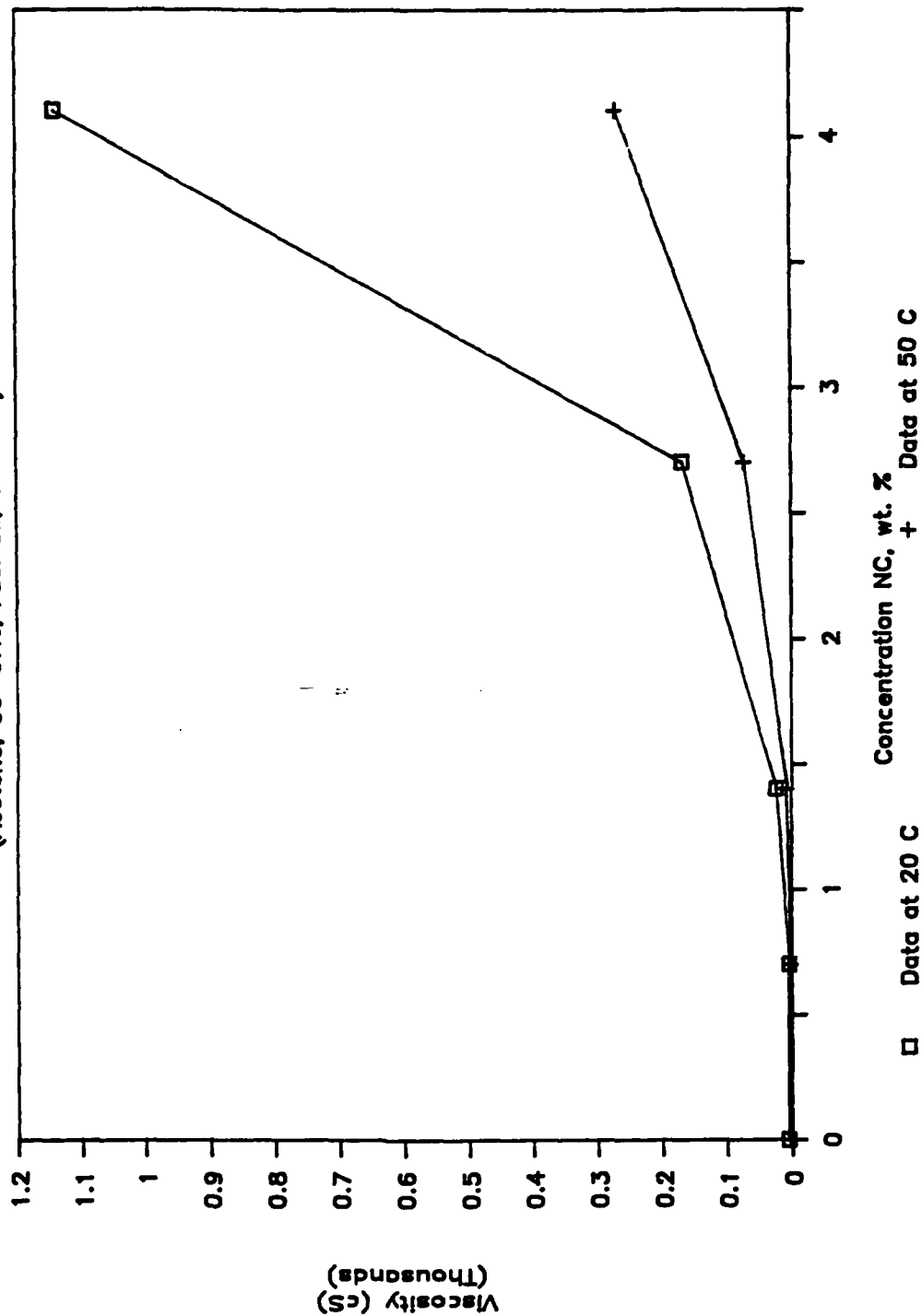


Figure 9. The Viscosities of Nitrocellulose (NC)-Acetone-No. 2 Fuel Oil Solutions at 20 and 50°C.



Similiar analyses could also be undertaken for the falling ball viscometer results obtained from the nitrocellulose-ethyl acetate-No. 2 fuel oil and nitrocellulose-butyl acetate-No. 2 fuel oil solutions at 20 and 50°C. However, these analyses would not be particularly informative since the economic analysis will show that ethyl acetate and butyl acetate are both significantly more expensive solvents than acetone. Therefore, only the estimated maximum concentrations of nitrocellulose in the ethyl acetate-No. 2 fuel oil and butyl acetate-No. 2 fuel oil solutions at 20 and 50°C will be given here.

The estimated maximum concentration refers to that value where the viscosity of the resulting solvent-No. 2 fuel oil-nitrocellulose solution will exceed the 30 centistoke limit required to efficiently atomize a fuel in an unmodified oil burner. For a ethyl acetate-No. 2 fuel oil solution at 20 and 50°C, the estimated maximum concentrations of nitrocellulose which could be tolerated are 0.9 and 1.5% by weight, respectively (Figure 10). These maximum concentrations of nitrocellulose in the ethyl acetate-No. 2 fuel oil solvent system are lower than those estimated for the nitrocellulose-acetone-No. 2 fuel oil mixtures (i.e., 1.5 and 1.8% nitrocellulose at 20 and 50°C, respectively) discussed above.

Finally, for the butyl acetate-No. 2 fuel oil solutions at 20 and 50°C, the estimated maximum concentrations of nitrocellulose which could be added before the 30 centistoke limit is exceeded are 1.1 and 1.2% by weight, respectively (Figure 11). Again, these maximum concentrations of

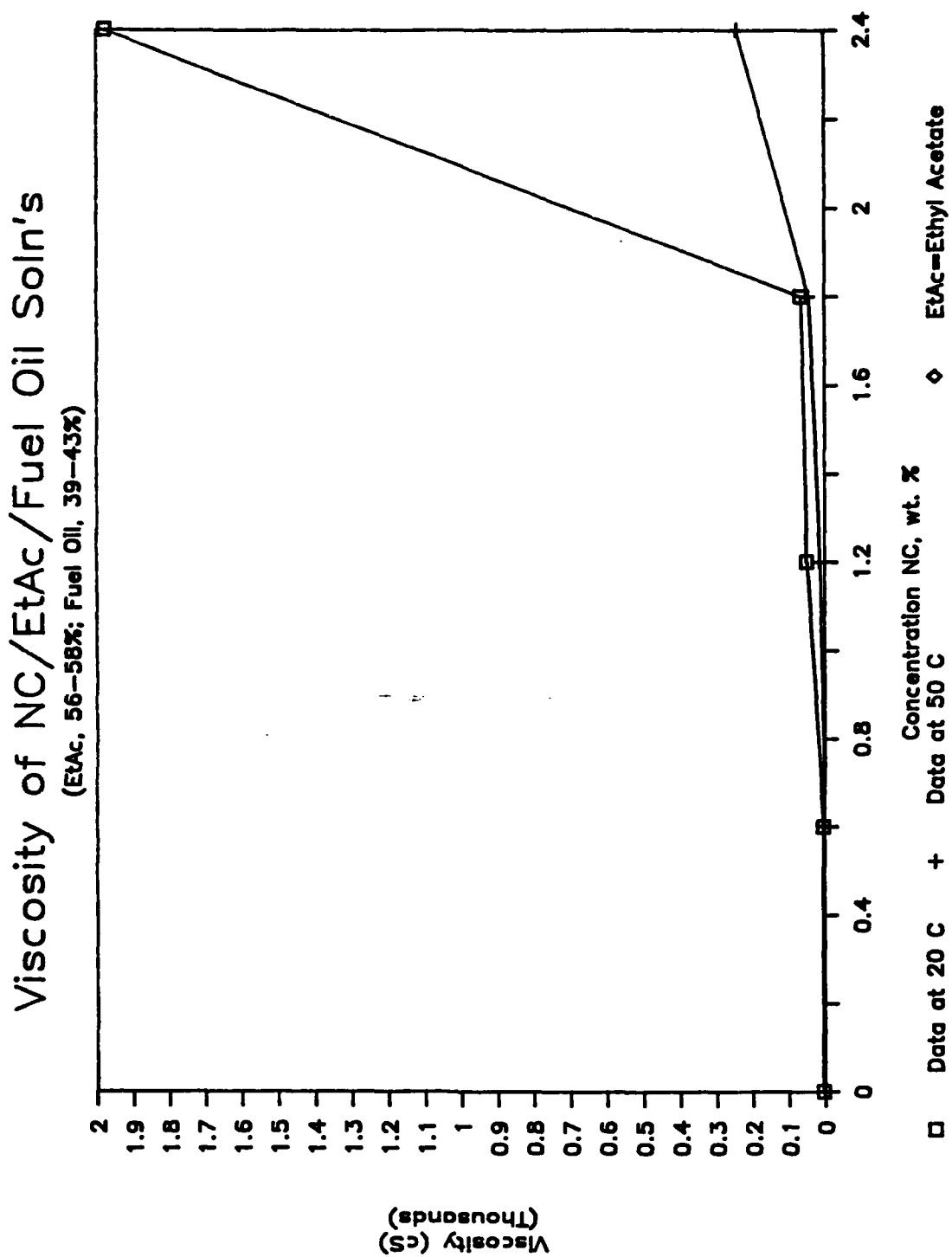


Figure 10. The Viscosities of Nitrocellulose (NC)-Ethyl Acetate-No. 2 Fuel Oil Solutions at 20 and 50°C.

# Viscosity of NC/BuAc/Fuel Oil Soln's

(BuAc, 39-44%; Fuel Oil, 54-61%)

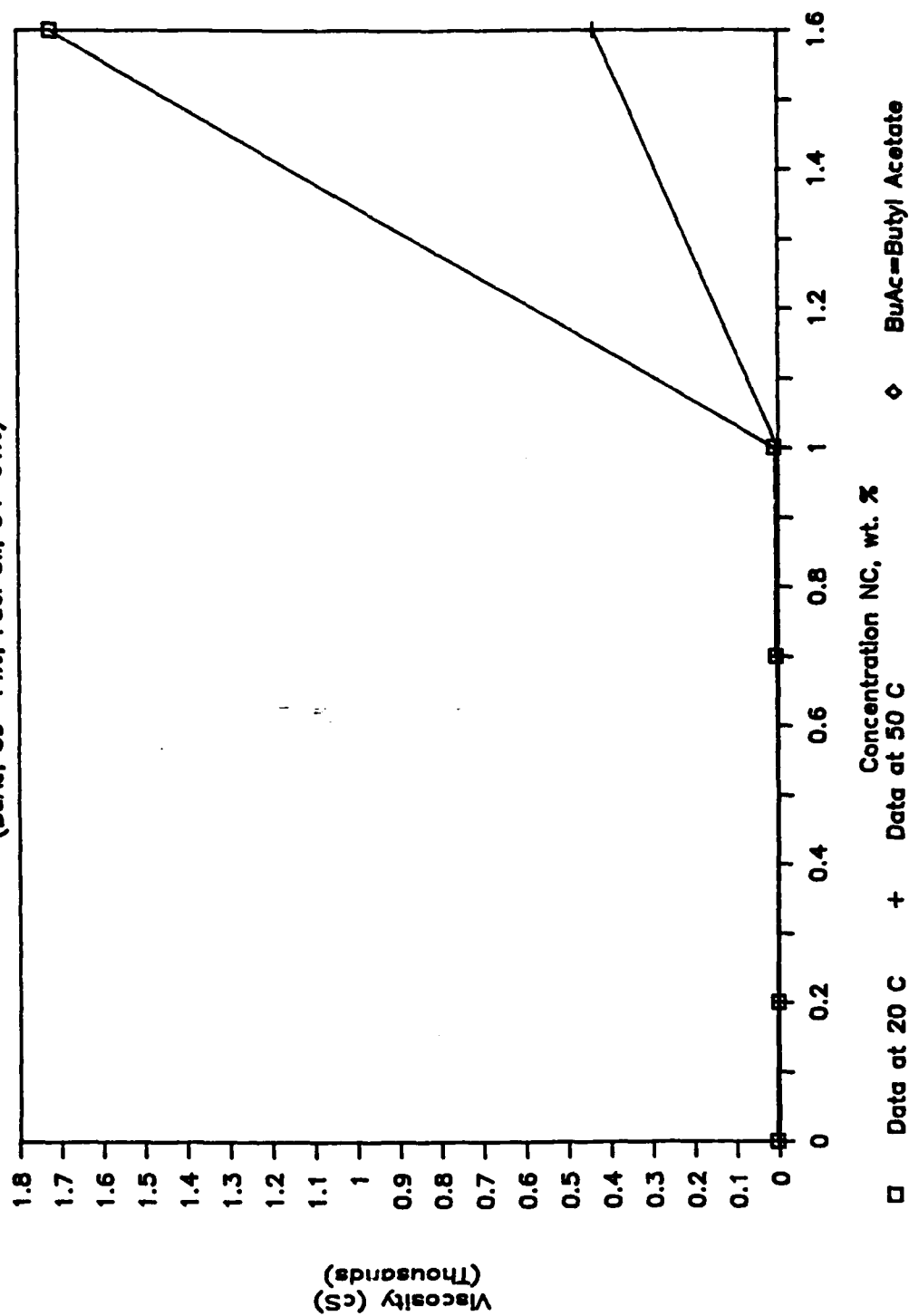


Figure 11. The Viscosities of Nitrocellulose (NC)-Butyl Acetate-No. 2 Fuel Oil Solutions at 20 and 50°C.

nitrocellulose in the butyl acetate-No. 2 fuel oil solvent system are lower than those estimated for the nitrocellulose-acetone-No. 2 fuel oil mixtures discussed above. Consequently, acetone appears to have the greatest "solvent power" for the 13.15% by weight nitrogen content, smokeless-grade nitrocellulose used in this study. In fact, acetone is also significantly less expensive than either ethyl acetate or butyl acetate. Therefore, the nitrocellulose-acetone-No. 2 fuel oil system will be the only one discussed later in the economic analysis.

#### 2.1.4.3 Results from Brookfield Viscometer

The results obtained from measurements of the viscosity of nitrocellulose-acetone solutions at 20°C with the Brookfield viscometer are given in Table 6. The viscosities of these solutions measured with the falling ball apparatus at 20°C are also given for comparison. Clearly, the viscosities measured with the falling ball and Brookfield viscometers are quite similar (average,  $\pm 2\%$ ). This was also found to be the case for the viscosities of the nitrocellulose-tetrahydrofuran, nitrocellulose-2-butanone, nitrocellulose-ethyl acetate, and nitrocellulose-butyl acetate solutions.

The viscosities of the nitrocellulose-solvent-No. 2 fuel oil mixtures were also measured with the Brookfield viscometer at 20 and 50°C, however, the results were not sufficiently different from those obtained with the falling ball apparatus to warrant additional comment here. The extent of shear thinning for these solutions was observed to be minimal.

Table 6. Viscosities of Nitrocellulose-Acetone Solutions at 20°C  
Measured by the Brookfield Viscometer

| <u>Solvent</u> | <u>Weight %<br/>Nitrocellulose</u> | <u>Spindle (No.)/Speed (rpm)</u> | <u>Viscosity<br/>(centistokes)</u> |
|----------------|------------------------------------|----------------------------------|------------------------------------|
| Acetone        | 2.1                                | 1/60                             | 18.5<br>(18.7) <sup>a</sup>        |
|                |                                    |                                  |                                    |
|                | 3.9                                | 1/6                              | 131.4                              |
|                |                                    | 1/12                             | 130.8                              |
|                |                                    | 1/30                             | 132.7                              |
|                |                                    |                                  | (125.2) <sup>a</sup>               |
|                | 5.8                                | 1/1.5                            | 524.1                              |
|                |                                    | 1/3                              | 536.5                              |
|                |                                    | 1/6                              | 537.7                              |
|                |                                    | 1/12                             | 543.3                              |
|                |                                    |                                  | (534.6) <sup>a</sup>               |
|                | 7.5                                | 3/12                             | 1791.8                             |
|                |                                    | 3/30                             | 1748.2                             |
|                |                                    | 3/60                             | 1723.9                             |
|                |                                    |                                  | (1723.9) <sup>a</sup>              |

<sup>a</sup>Viscosity of solution measured with the falling ball apparatus  
at 20°C.

## 2.2 CHEMICAL CHARACTERISTICS OF NITROCELLULOSE-SOLVENT- NO. 2 FUEL OIL MIXTURES

The second series of tests in this project were conducted to  
determine the chemical characteristics of nitrocellulose-solvent and

nitrocellulose-solvent-No. 2 fuel oil mixtures. Flash points, fire points, and heats of combustion of No. 2 fuel oil, as well as the nitrocellulose-solvent and nitrocellulose-solvent-No. 2 fuel oil mixtures were determined in this phase of the project. In each section which follows, an introduction will again be given to provide the background information required to intelligently discuss the results obtained from each test.

### 2.2.1 Flash Point Tests

#### 2.2.1.1 Introduction

The flash point measures the tendency of a sample to form a flammable mixture with air under controlled laboratory conditions. It is one of the important properties which must be considered in assessing the overall flammability hazard of a material. Flash point is used in shipping and safety regulations to define "flammable" materials. Three degrees of flammability are commonly used: flammable, combustible and nonflammable. They are defined as follows:

Flammable - flash point is less than 100°F,

Combustible - flash point is measurable and greater than 100°F, and

Nonflammable - flash point is not measurable.

The flash point can also indicate the possible presence of a highly volatile and flammable component in an apparently nonvolatile or nonflammable material. The following section describes the results obtained from the determination of the flash points of solvents, No. 2 fuel oil, solvent-No. 2 fuel oil, and nitrocellulose-solvent-No. 2 fuel oil mixtures according to ASTM D93-85 standard procedure.

#### 2.2.1.2 Results and Discussion

The flash points of solvents (acetone, ethyl acetate, tetrahydrofuran, 2-butanone, and butyl acetate), No. 2 fuel oil, No. 2 fuel oil-solvent, and selected nitrocellulose-solvent-No. 2 fuel oil mixtures are summarized in Table 7. The various solvent-No. 2 fuel oil and nitrocellulose-solvent-No. 2 fuel oil combinations investigated in these tests were based on the results obtained from the dilution ratio experiments (Table 1). For each dilution ratio test, the weight percent content of nitrocellulose, No. 2 fuel oil and solvent was calculated for each final test mixture, and these data were used to prepare the solutions used for the flash point tests.

The results shown in Table 7 indicate that for ethyl acetate, butyl acetate, tetrahydrofuran, and 2-butanone, the flash point of the solvent-No. 2 fuel oil solution is higher than the flash point of the solvent alone. On the other hand, the flash points for the acetone-No. 2 fuel oil mixtures are lower than the flash point for acetone alone.

Table 7. Flash Points<sup>a</sup> of Solvents, No. 2 Fuel Oil, Solvent-No. 2 Fuel Oil, and Selected Nitrocellulose (NC)-Solvent-No. 2 Fuel Oil Mixtures<sup>b</sup>

| <u>Solvent</u>   | <u>Weight %<br/>Solvent</u> | <u>Weight %<br/>Fuel Oil</u> | <u>Weight %<br/>NC</u> | <u>Flash<br/>Point (°F)</u> |
|------------------|-----------------------------|------------------------------|------------------------|-----------------------------|
| Fuel Oil         | 0.0                         | 100.0                        | 0.0                    | 178                         |
| Acetone          | 100.0                       | 0.0                          | 0.0                    | -4                          |
|                  | 70.0                        | 30.0                         | 0.0                    | -4                          |
|                  | 60.0                        | 40.0                         | 0.0                    | -13                         |
|                  | 66.5                        | 32.1                         | 1.4                    | 0                           |
|                  | 70.7                        | 23.5                         | 5.8                    | -12                         |
| Ethyl<br>Acetate | 100.0                       | 0.0                          | 0.0                    | 33                          |
|                  | 60.0                        | 40.0                         | 0.0                    | 34                          |
|                  | 50.0                        | 50.0                         | 0.0                    | 36                          |
|                  | 40.0                        | 60.0                         | 0.0                    | 36                          |
|                  | 58.1                        | 39.5                         | 2.4                    | 23                          |
| Butyl<br>Acetate | 100.0                       | 0.0                          | 0.0                    | 82                          |
|                  | 45.0                        | 55.0                         | 0.0                    | 91                          |
|                  | 35.0                        | 65.0                         | 0.0                    | 97                          |
|                  | 39.0                        | 60.4                         | 0.6                    | 93                          |
| THF <sup>c</sup> | 100.0                       | 0.0                          | 0.0                    | 6                           |
|                  | 55.0                        | 45.0                         | 0.0                    | 12                          |
|                  | 45.0                        | 55.0                         | 0.0                    | 19                          |
| 2-Butanone       | 100.0                       | 0.0                          | 0.0                    | 25                          |
|                  | 55.0                        | 45.0                         | 0.0                    | 32                          |
|                  | 45.0                        | 55.0                         | 0.0                    | 32                          |

<sup>a</sup>Measured according to ASTM D93-85 standard procedure.

<sup>b</sup>No. 2 fuel oil-solvent and No. 2 fuel oil-solvent-nitrocellulose combinations investigated were based on results from the dilution ratio experiments (Table 1).

<sup>c</sup>THF = tetrahydrofuran.



In general, addition of nitrocellulose to the various solvent-No. 2 fuel oil mixtures listed in Table 7 results in a slight decrease in the value of the flash point. Finally, the data summarized in Table 7 clearly shows that each solvent-No. 2 fuel oil and nitrocellulose-solvent-No. 2 fuel oil mixture may be classified as "flammable".

#### 2.2.2 Fire Point Tests

##### 2.2.2.1 Introduction

The fire point measures the characteristics of a sample which are required to support combustion. The fire point is defined as the lowest temperature at which a volatile combustible substance vaporizes rapidly enough to form above its surface an air-vapor mixture which burns continuously when ignited by a small flame. The results obtained from fire point determinations of solvents, No. 2 fuel oil, solvent-No. 2 fuel oil, and nitrocellulose-solvent-No. 2 fuel oil mixtures according to ASTM D92-85 standard procedure are discussed in the following section.

##### 2.2.2.2 Results and Discussion

The fire points of solvents (acetone, ethyl acetate, tetrahydrofuran, 2-butanone, and butyl acetate), No. 2 fuel oil, No. 2 fuel oil-solvent and selected nitrocellulose-solvent-No. 2 fuel oil mixtures are summarized in Table 8. The various solvent-No. 2 fuel oil and

Table 8. Fire Points<sup>a</sup> of Solvents, No. 2 Fuel Oil, Solvent-No. 2 Fuel Oil, and Selected Nitrocellulose (NC)-Solvent-No. 2 Fuel Oil Mixtures<sup>b</sup>

| <u>Solvent</u>   | <u>Weight %<br/>Solvent</u> | <u>Weight %<br/>Fuel Oil</u> | <u>Weight %<br/>NC</u> | <u>Fire<br/>Point (°F)</u> |
|------------------|-----------------------------|------------------------------|------------------------|----------------------------|
| Fuel Oil         | 0.0                         | 100.0                        | 0.0                    | 237                        |
| Acetone          | 100.0                       | 0.0                          | 0.0                    | -2                         |
|                  | 70.0                        | 30.0                         | 0.0                    | 14                         |
|                  | 60.0                        | 40.0                         | 0.0                    | 7                          |
|                  | 66.5                        | 32.1                         | 1.4                    | -8                         |
|                  | 70.7                        | 23.5                         | 5.8                    | -4                         |
| Ethyl<br>Acetate | 100.0                       | 0.0                          | 0.0                    | 46                         |
|                  | 60.0                        | 40.0                         | 0.0                    | 41                         |
|                  | 50.0                        | 50.0                         | 0.0                    | 36                         |
|                  | 40.0                        | 60.0                         | 0.0                    | 39                         |
|                  | 58.1                        | 39.5                         | 2.4                    | 36                         |
| Butyl<br>Acetate | 100.0                       | 0.0                          | 0.0                    | 95                         |
|                  | 45.0                        | 55.0                         | 0.0                    | 100                        |
|                  | 35.0                        | 65.0                         | 0.0                    | 108                        |
|                  | 39.0                        | 60.4                         | 0.6                    | 82                         |
| THF <sup>c</sup> | 100.0                       | 0.0                          | 0.0                    | 16                         |
|                  | 55.0                        | 45.0                         | 0.0                    | 16                         |
|                  | 45.0                        | 55.0                         | 0.0                    | 7                          |
| 2-Butanone       | 100.0                       | 0.0                          | 0.0                    | 36                         |
|                  | 55.0                        | 45.0                         | 0.0                    | 39                         |
|                  | 45.0                        | 55.0                         | 0.0                    | 39                         |

<sup>a</sup>Measured according to ASTM D92-85 standard procedure.

<sup>b</sup>No. 2 fuel oil-solvent and No. 2 fuel oil-solvent-nitrocellulose combinations investigated were based on results from the dilution ratio experiments (Table 1).

<sup>c</sup>THF = tetrahydrofuran.

nitrocellulose-solvent-No. 2 fuel oil combinations investigated in these tests were again based on the results obtained from the dilution ratio experiments (Table 1). These combinations were calculated and prepared as described in the previous section.

The results shown in Table 8 indicate that for acetone, butyl acetate, and 2-butanone, the fire points of the solvent-No. 2 fuel oil solutions are higher than the solvents alone. On the other hand, the opposite is true for ethyl acetate and tetrahydrofuran containing additions of No. 2 fuel oil. Furthermore, addition of nitrocellulose to the four solvent-No. 2 fuel oil mixtures listed in Table 8 results in a decrease in the value of the fire point. It had previously been a matter of some concern, expressed in the test plan for this project, that measurement of the fire points of nitrocellulose-solvent-No. 2 fuel oil mixtures might not be possible due to safety considerations. However, during the analysis of these nitrocellulose-solvent-No. 2 fuel oil mixtures, the observation was made that these nitrocellulose-containing mixtures burned in an identical manner to the solvent-No. 2 fuel oil mixtures.

#### 2.2.3 Heat of Combustion Tests

The heat of combustion is a measure of the energy released when 1 mol of a substance is oxidized at constant pressure or constant volume. A knowledge of this value is essential when considering the thermal efficiency of equipment for producing either power or heat.

### 2.2.3.1 Introduction

Nitrocellulose, as the major ingredient of smokeless powder, occupies a key position in the field of solid propellants. The heats of combustion, as well as the heats of explosion, of nitrocelluloses prepared from cotton linters and wood pulp, and with various nitrogen contents have been reported by Taylor and Hall<sup>10</sup>, and by Jessup and Prosen<sup>11</sup>. The latter authors give heats of combustion measured at 30°C with a bomb calorimeter of one sample of cellulose and four samples of nitrocellulose prepared from cotton linters, as well as one sample of cellulose and four samples of nitrocellulose prepared from wood pulp. These heat of combustion measurements are summarized in Table 9.

Table 9. Heats of Combustion<sup>a</sup> of Cellulose, Dinitrocellulose, and Trinitrocellulose from Cotton Linters and Wood Pulp

| <u>Material</u>   | <u>Source of Cellulose</u> | <u>Heat of Combustion (Btu/lb)</u> |
|-------------------|----------------------------|------------------------------------|
| Cellulose         | Cotton Linters             | 7497                               |
|                   | Wood Pulp                  | 7511                               |
| Dinitrocellulose  | Cotton Linters             | 4706                               |
|                   | Wood Pulp                  | 4710                               |
| Trinitrocellulose | Cotton Linters             | 3943                               |
|                   | Wood Pulp                  | 3940                               |

<sup>a</sup>Heat of Combustion Data from Ref. 10.

There are two important points to note based on the data given in Table 9. First, although there are significant differences between the heats of combustion of cellulose from cotton linters and from woodpulp, 0.18%, and between the nitrocelluloses from cotton linters and from woodpulp, maximum 0.1%, Jessup and Prosen felt that this probably did not indicate a real difference in the heats of combustion of pure cellulose or of nitrocelluloses from cotton linters or woodpulp. Rather, the differences were judged to be an indication that the impurities in the materials made some contribution to the heat of combustion. Consequently, it is assumed that the heat of combustion data obtained from the smokeless-grade nitrocellulose sample, derived from woodpulp, used in this study, as well as the solvent-No. 2 fuel oil mixtures containing this nitrocellulose, should provide an accurate estimate of the heat of combustion to be expected if a supplemental fuel consisting of a military-grade nitrocellulose (prepared from cotton linters) dissolved in a solvent and further mixed with No. 2 fuel oil were used to fire a boiler. Second, the heat of combustion actually decreases as the degree of nitration of the cellulose polymer increases, with the heat of combustion for trinitrocellulose (14.15% nitrogen) derived from woodpulp, for example, being 3571 Btu/lb less than the heat of combustion for cellulose derived from woodpulp.

### 2.2.3.2 Results and Discussion

The heat of combustion data obtained from the smokeless-grade nitrocellulose, solvents, No. 2 fuel oil, and nitrocellulose-solvent-No. 2 fuel oil mixtures according to ASTM D240-87 standard procedure are given in Table 10. The agreement between the actual and calculated (given in parenthesis) heat of combustion values for the nitrocellulose-solvent-No. 2 fuel oil mixtures is quite good. Based on this fact, it is assumed that the economic analyses of the various nitrocellulose-No. 2 fuel oil and nitrocellulose-acetone-No. 2 fuel oil mixtures given in section 3.2 are reasonably accurate.

Table 10. Heats of Combustion for Nitrocellulose, Solvents, No. 2 Fuel Oil, and Selected Nitrocellulose-Solvent-No. 2 Fuel Oil Mixtures

| <u>Material</u>  | <u>Heat of Combustion (Btu/lb)</u> |
|--|------------------------------------|
| Smokeless-Grade Nitrocellulose (NC)<br>(Hercules, Grade C, Type 1) | 4100                               |
| Acetone  | 13229                              |
| Ethyl Acetate  | 10980                              |
| No. 2 Fuel Oil   | 19500                              |
| 5.8% NC-70.7% Acetone-23.5% Fuel Oil                               | 13970 (14175)                      |
| 1.4% NC-66.5% Acetone-32.1% Fuel Oil                               | 15005 (15115)                      |
| 2.4% NC-58.1% Ethyl Acetate-39.5% Fuel Oil                         | 14345 (14181)                      |

## 2.3 CHEMICAL COMPATABILITY OF NITROCELLULOSE-SOLVENT- NO. 2 FUEL OIL MIXTURES

The third and final series of laboratory tests in this project were conducted to determine the chemical compatibility of nitrocellulose-solvent and nitrocellulose-solvent-No. 2 fuel oil mixtures. The chemical compatibility of these mixtures was evaluated using a thermal analysis technique, differential scanning calorimetry, as well as additional qualitative analyses. The discussion of the results obtained from each series of tests is prefaced by an introductory section.

### 2.3.1 Differential Scanning Calorimetry (DSC)

#### 2.3.1.1 Introduction

The thermal decomposition of nitrocellulose has been studied for many years<sup>7</sup>. Wolfrom et al.<sup>12</sup> analyzed the decomposition products from nitrocellulose by assuming that the thermally initiated rupture of the cellulose nitrate molecule gave a series of volatile species whose relative importance was inversely proportional to the pressure of the system. Later, using spectroscopic and gravimetric techniques, Phillips et al.<sup>13</sup> showed that the thermal decomposition of nitrocellulose follows, in first approximation, first-order kinetics with two or three branches, suggesting that a more complex reaction process than a simple first-order one might occur.

More recently, Pfeil and Eisenreich<sup>14</sup> studied the thermal decomposition of nitrocellulose by thermogravimetric analysis, differential thermal analysis, and infrared and Raman spectroscopies. Their results revealed the presence of an initial autocatalytic decomposition of nitrate groups and an increase in carbonyl and hydroxyl groups up to a weight loss of 55%. Further decomposition turned out to be a second-order reaction, terminating in a charcoal-like residue.

Lemieux and Prud'homme<sup>15</sup> used a DSC apparatus to compare the heats of decomposition of seven nitrocellulose samples, derived from wood and cotton, with various nitrogen contents ranging from 12.6 to 13.5%. Heats of decomposition of nitrocellulose-acetone, nitrocellulose-tetrahydrofuran and nitrocellulose-ethyl acetate samples were also measured. Lemieux and Prud'homme observed that the average heat of decomposition of nitrocellulose samples increased slightly with nitrogen content, the values ranging between 1711 and 2050 J g<sup>-1</sup>. A comparison of the two types of nitrocellulose from woodpulp and cotton linters showed that the heats of decomposition were quite similar at low nitrogen contents. However, when the nitrogen content of each type of nitrocellulose increased, heats of decomposition obtained for samples of nitrocellulose derived from woodpulp were slightly higher than those measured for cotton linters.

Lemieux and Prud'homme also clearly demonstrated the effect of three solvents (acetone, tetrahydrofuran, and ethyl acetate) on the thermal



decomposition of nitrocellulose. The heats of decomposition of nitrocellulose-acetone and nitrocellulose-tetrahydrofuran samples increased as the nitrogen content of the nitrocellulose increased. In the case of the nitrocellulose-ethyl acetate samples, the heats of decomposition increased slightly as the nitrogen content of the nitrocellulose derived from woodpulp increased, whereas there was almost no variation in heats of decomposition for nitrocellulose derived from cotton linters as the nitrogen content of this material increased. They reasoned that this unique behavior of nitrocellulose samples cast from ethyl acetate could enable one to differentiate cotton samples from woodpulp samples, since these two types of nitrocellulose samples exhibited significantly different heat of decomposition values.

In addition to the DSC analyses for nitrocellulose described above, the thermal decomposition of propellants can be conveniently analyzed using DSC. For example, House et al.<sup>16</sup> used DSC to compare the decomposition of twelve commercial nitrocellulose-containing propellants. Curiously, these researchers observed two different decomposition pathways for the same propellant, even though each DSC experiment was run in the same fashion. The first decomposition pattern may be represented by the following:

$$\text{Propellant} = \text{volatile products} + 12\text{-}16\% \text{ residue} \quad (1)$$

while the second decomposition pattern is represented by

$$\text{Propellant} = \text{volatile products} + 2\text{-}5\% \text{ residue} \quad (2)$$

The results obtained by House et al. indicated that there was no significant difference between the heats of decomposition of most propellants investigated which decompose according to Equation 1. However, for some propellants, decomposition could take place by Equation 1 or 2 with about equal frequency.

#### 2.3.1.2 Results and Discussion

A typical DSC curve obtained from decomposition of the smokeless-grade nitrocellulose sample is given in Figure 12. A Perkin-Elmer DSC-7 instrument was used to obtain the DSC curve according to ASTM E537-86 standard procedure. Figure 12 shows that the exothermic decomposition peak is asymmetric with decomposition starting at about 177°C and finishing at about 257°C, with the peak maximum located at about 217°C. DSC curves were also obtained from thin films of material cast from nitrocellulose-acetone-No. 2 fuel oil, nitrocellulose-ethyl acetate-No. 2 fuel oil, and nitrocellulose-butyl acetate-No. 2 fuel oil mixtures. In each case, only a slight increase in the average heat of

decomposition for the nitrocellulose-solvent-No. 2 fuel oil mixtures over the average heat of decomposition for nitrocellulose itself was noted. Therefore, it is possible to change the decomposition behavior of nitrocellulose slightly by exposing the sample to a solvent mixture which is likely to be retained to some degree by the nitrocellulose molecule.

DSC Curve for Nitrocellulose  
(ASTM E 537-86)

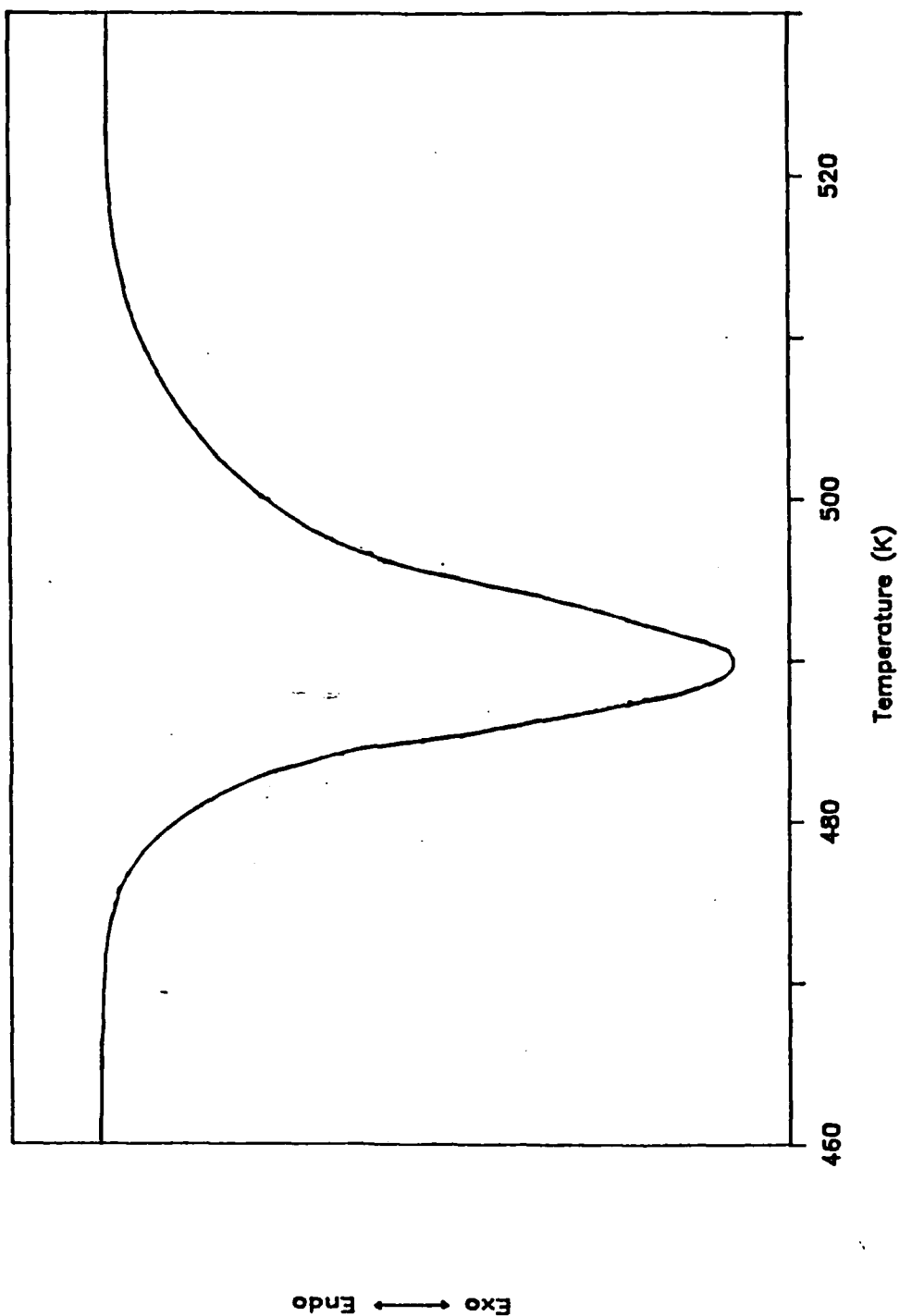


Figure 12. Differential Scanning Calorimetry Curve for the Decomposition of a Smokeless-Grade Nitrocellulose

### 2.3.2 Supplementary Tests

#### 2.3.2.1 Introduction

Qualitative analyses of nitrocellulose-solvent and nitrocellulose-solvent-No. 2 fuel oil solutions were conducted over the six month course of this project to determine if any color changes, separation of solution phases, or precipitation occurred.

#### 2.3.2.2 Nitrocellulose-Solvent Mixtures

Solutions of acetone containing 1.0-7.5% by weight nitrocellulose, ethyl acetate containing 1.0-4.8% by weight nitrocellulose, tetrahydrofuran containing 1.0-6.6% by weight nitrocellulose, butyl acetate containing 0.5-4.4% by weight nitrocellulose, and 2-butanone containing 1.0-6.6% by weight nitrocellulose were prepared in 2 oz. glass bottles and stored on a shelf in the laboratory at ambient temperature. After five months, all of the solutions are still free of any precipitate. However, the color of the 2-butanone-nitrocellulose and tetrahydrofuran-nitrocellulose solutions progressed from transparent when freshly prepared, to yellow after approximately one week, to an orange-red color after approximately one month with no additional color change occurring after five months of storage. Furthermore, the color of the acetone-nitrocellulose solutions progressed from transparent when freshly prepared to a pale yellow shading after five months storage. On

the other hand, no discoloration of the ethyl acetate-nitrocellulose or butyl acetate-nitrocellulose solutions was noted over a storage period of five months.

The light-sensitive nature of various solutions containing nitrocellulose was first noticed in the course of the early investigations of both nitrocellulose and propellant powders. For instance, Abel<sup>17</sup> observed in 1867 that nitrocellulose exposed to strong light eventually became acid and was converted into a brown, gum-like mass. Nitric, formic, and oxalic acids, cyanogen, and glucose could be extracted from this gum-like mass with water. Subsequent investigations have yielded little noteworthy information on the nature of the photodecomposition mechanism for nitrocellulose. However, since a batch process would likely be used to burn the supplemental fuel containing nitrocellulose, the photo-decomposition reaction which does occur in various solvents should not present any problem.

#### 2.3.2.3 Nitrocellulose-Solvent-No. 2 Fuel Oil Mixtures

No. 2 fuel oil was gradually added to solutions of acetone containing 1.0-7.5% by weight nitrocellulose, ethyl acetate containing 1.0-4.8% by weight nitrocellulose, and butyl acetate containing 0.5-4.4% by weight nitrocellulose. The final concentrations of nitrocellulose in each solvent-No. 2 fuel oil-nitrocellulose mixture, as well as the qualitative observations made of these mixtures, are given in Table 11. These observations were made over a time period of three days.

For each solvent, at the lowest concentrations of nitrocellulose (0.2-1.2% by weight), either none or only a small amount of precipitation was observed in the solvent-No. 2 fuel oil-nitrocellulose mixture after three days. For the nitrocellulose-acetone-No. 2 fuel oil mixtures containing 1.4-5.6% by weight nitrocellulose, significant amounts of the nitrocellulose precipitated from solution as a gel-like mass on the bottom of the container over the three days observation period. This precipitate was difficult to redisperse when the mixture was agitated vigorously by hand. The same general observations were also made for the nitrocellulose-ethyl acetate-No. 2 fuel oil and nitrocellulose-butyl acetate-No. 2 fuel oil mixtures containing elevated levels of nitrocellulose; these observations are detailed in Table 11.

At this point in the project, the accumulated technical data and preliminary results from the economic analysis strongly indicated that acetone would be the solvent of choice for a supplemental fuel composed of nitrocellulose, solvent, and No. 2 fuel oil. Since the initial qualitative tests had revealed that nitrocellulose would precipitate from various nitrocellulose-acetone-No. 2 fuel oil mixtures upon standing for three days, another set of nitrocellulose-acetone-No. 2 fuel oil mixtures, identical to those listed in Table 11, was prepared. However, these samples were placed on a reciprocating shaker on low speed. In this case, these samples remained free of precipitate for at least one month, at which time the experiment was terminated. Therefore, either mechanical agitation or constant air-sparging would be required if batches of nitrocellulose-acetone-No. 2 fuel oil mixtures were to be stored for any period of time before being fed to a burner as a supplemental fuel.

Table 11. Supplementary Tests: Qualitative Observations of Nitrocellulose (NC)-Solvent-No. 2 Fuel Oil Mixtures<sup>a</sup>

| <u>Solvent</u>   | <u>Wt. %<br/>Solvent</u> | <u>Wt. %<br/>Fuel Oil</u> | <u>Wt. %<br/>NC</u> | <u>Comments</u>  |
|------------------|--------------------------|---------------------------|---------------------|--|
| Acetone          | 65.6                     | 33.7                      | 0.7                 | Small amount of gel precipitate, disperses easily with agitation   |
| Acetone          | 66.5                     | 32.1                      | 1.4                 | Larger amount of gel precipitate, adheres strongly to bottom of container and does not redisperse easily with agitation. Amount of gel precipitate increases as the wt. % of NC in the mixture increases |
|                  | 66.4                     | 30.9                      | 2.7                 |  |
|                  | 66.2                     | 29.6                      | 4.2                 |  |
|                  | 68.5                     | 25.9                      | 5.6                 |  |
| Ethyl<br>Acetate | 56.4                     | 43.0                      | 0.6                 | Small amount of gel precipitate, disperses easily with agitation   |
|                  | 58.5                     | 40.3                      | 1.2                 |  |
|                  | 56.5                     | 41.7                      | 1.8                 | Large amount of gel precipitate, disperses easily with agitation but particles adhere to inside wall of the container  |
|                  | 58.1                     | 39.5                      | 2.4                 |  |
|                  | 61.4                     | 35.5                      | 3.1                 | Thick, gel-like solution which easily disperses to a homogeneous solution with agitation. No gel particles adhere to container   |
|                  |                          |                           |                     |  |
| Butyl<br>Acetate | 38.9                     | 60.9                      | 0.2                 | Clear, fluid solution; no precipitation visible  |
|                  | 39.0                     | 60.4                      | 0.6                 |  |
|                  | 40.2                     | 58.8                      | 1.0                 | Mixture begins to thicken; gel-like mass coats the inside of the container. Coating thickens and gel particles appear as the wt. % NC in the mixture increases   |
|                  | 44.4                     | 54.0                      | 1.6                 |  |
|                  | 49.2                     | 48.5                      | 2.3                 |  |

<sup>a</sup>After standing at room temperature for three days.



### 3. ECONOMIC ANALYSIS

An economic analysis of the various solvents, No. 2 fuel oil, and solvent-nitrocellulose-No. 2 fuel oil mixtures was performed in this phase of the project. This analysis emphasizes the cost of the solvents, No. 2 fuel oil, and solvent-No. 2 fuel oil mixtures as well as the amount of nitrocellulose that could be dissolved in each solvent-No. 2 fuel oil mixture.

#### 3.1 SOLVENTS AND ACETONE-NITROCELLULOSE-NO. 2 FUEL OIL MIXTURES

##### 3.1.1 Initial Cost Comparison of Solvents

To begin the economic analysis, the prices of the five candidate solvents for nitrocellulose identified in the literature search (section 6.1) were obtained from the Chemical Marketing Reporter (Vol. 235, No. 5, January 29, 1990 issue). These prices, which are based on railroad tankcar deliveries of each solvent, are as follows:

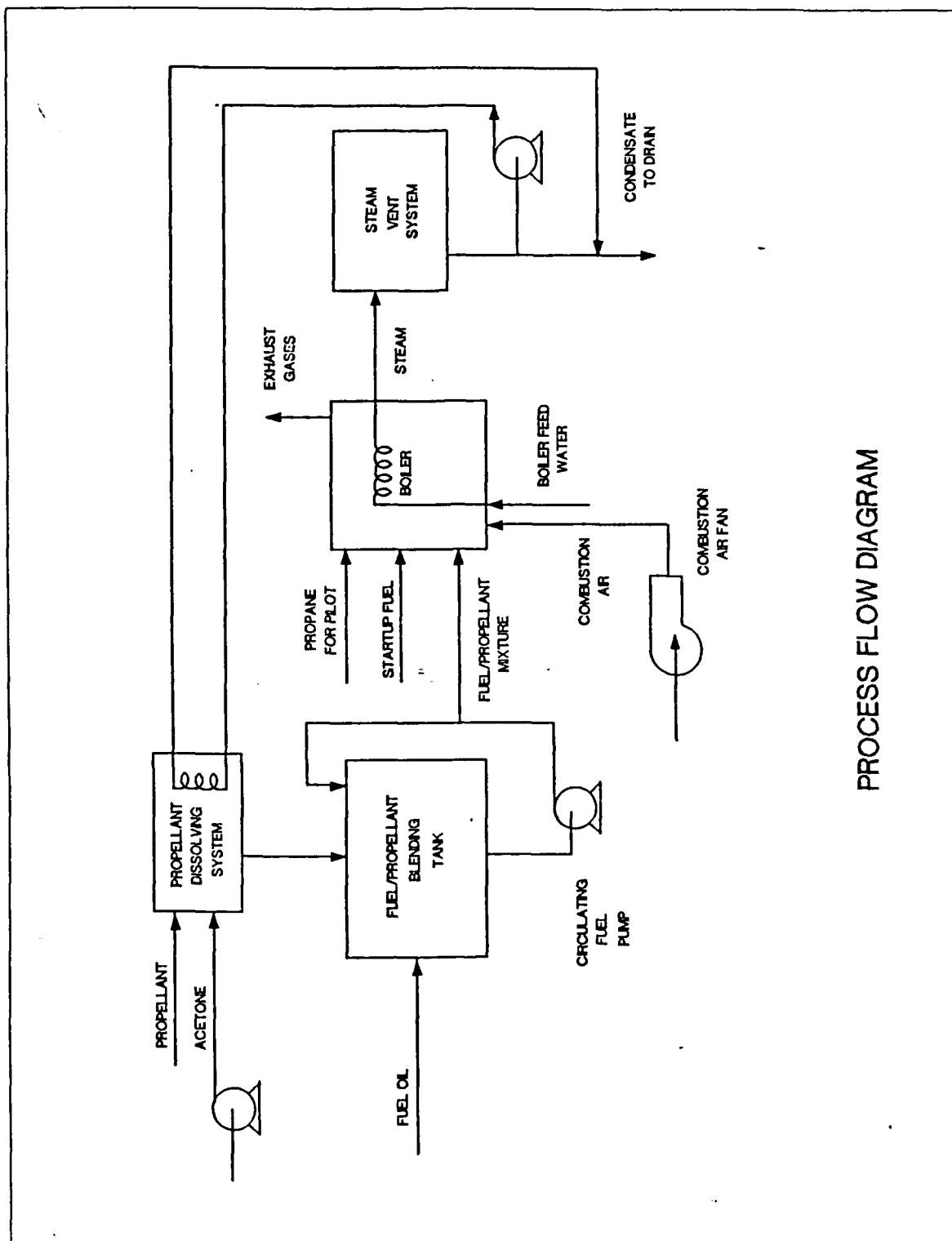
| <u>Solvent</u>  | <u>Cost (\$/lb)</u> |
|-----------------|---------------------|
| Acetone         | 0.30                |
| 2-Butanone      | 0.30                |
| Butyl Acetate   | 0.43                |
| Ethyl Acetate   | 0.41                |
| Tetrahydrofuran | 1.20                |

At this point, tetrahydrofuran was eliminated from further consideration in this analysis for two reasons. First, the cost of the chemical was three to four times more than the other four solvents. Second, tetrahydrofuran did not exhibit any outstanding physical characteristics with the nitrocellulose, as was clearly demonstrated in the previous sections concerning the results from the laboratory tests. In addition, 2-butanone was eliminated from further consideration for similar reasons. First, 2-butanone did not exhibit any outstanding physical characteristics with the nitrocellulose. Second, and perhaps more importantly, this solvent is listed as an Environmental Protection Agency (EPA) toxic substance.

Next, the costs of the three remaining solvents were compared. Acetone was obviously the least expensive solvent for nitrocellulose when compared to ethyl and butyl acetate. Furthermore, in addition to the economic advantage, acetone was able to dissolve a greater concentration of nitrocellulose (7.5%) than either butyl acetate (4.4%) or ethyl acetate (4.8%). Therefore, acetone was determined to be the most economical and technically suitable solvent for nitrocellulose.

### 3.1.2 Results and Discussion

The process flow diagram for burning a No. 2 fuel oil-acetone-nitrocellulose mixture in a boiler is shown in Figure 13.



PROCESS FLOW DIAGRAM

Figure 13. Process Flow Diagram for Burning a Supplemental Fuel

The costs for burning a No. 2 fuel oil-acetone-nitrocellulose mixture compared with burning No. 2 fuel oil only was determined for two mixtures containing different concentrations of nitrocellulose. The cost comparison was based on the prices of acetone and No. 2 fuel oil (\$0.10/lb), the cost of storing nitrocellulose, and the cost for disposing of nitrocellulose by incineration. Equipment costs were not considered in this analysis.

The weight percent compositions of the mixtures chosen, 64.6% acetone-31.2% No. 2 fuel oil-4.2% nitrocellulose and 64.8% acetone-29.3% No. 2 fuel oil-5.9% nitrocellulose, were based on the data (Table 1) obtained from the dilution ratio experiments discussed in section 2.1.1.2. To begin the economic analysis for each mixture, the heat of combustion was calculated. Next, the quantity of each mixture required to fuel each of four different boiler sizes (i.e., 20, 30, 40, and 50 MBtu/hr) was determined. Finally, the costs for the burning each mixture in the quantities required to fuel each boiler were calculated and compared to the costs required to fuel the boilers with No. 2 fuel oil only. These comparisons are shown in Table 12 and the equations used to calculate each quantity are given in Appendix C.

The data given in Table 12 clearly shows that in both cases, substantial additional costs will be incurred if the Army's boilers are fueled with a No. 2 fuel oil-acetone-nitrocellulose mixture instead of No. 2 fuel oil alone. For example, the additional costs to burn the

Table 12. Comparison<sup>a</sup> Between Burning No. 2 Fuel Oil Versus a No. 2 Fuel Oil-Acetone-Nitrocellulose (NC) Mixture

Part A

Weight percent of NC in the mixture<sup>b</sup> = 4.2%

Dilution ratio of the mixture<sup>b</sup> = 0.443

Weight percent composition of the mixture<sup>b</sup>: 31.2% No. 2 fuel oil, 64.6% acetone, and 4.2% nitrocellulose

Heat of combustion for the mixture<sup>b</sup> = 14803 Btu/lb

| Boiler size, MBtu/hr | Mixture input, lb/hr (gpm) <sup>c</sup> | Cost to burn mixture, \$/hr | Cost to burn fuel oil only, \$/hr | Additional cost to burn mixture over fuel oil, \$/hr | Amount of NC consumed, metric tons/yr |
|----------------------|---|-----------------------------|-----------------------------------|--|---------------------------------------|
| 20                   | 1351 (3)                                | 318                         | 107                               | 211  | 225                                   |
| 30                   | 2027 (5)                                | 477                         | 160                               | 317  | 338                                   |
| 40                   | 2702 (7)                                | 635                         | 213                               | 422  | 451                                   |
| 50                   | 3378 (8)                                | 794                         | 267                               | 528  | 564                                   |

Part B

Weight percent of NC in the mixture<sup>b</sup> = 5.9%

Dilution ratio of the mixture<sup>b</sup> = 0.414

Weight percent composition of the mixture<sup>b</sup> = 29.3% No. 2 fuel oil, 64.8% acetone, 5.9% nitrocellulose

Heat of combustion for the mixture<sup>b</sup> = 14526 But/lb

| Boiler size, MBtu/hr | Mixture input, lb/hr (gpm) <sup>c</sup> | Cost to burn mixture, \$/hr | Cost to burn fuel oil only, \$/hr | Additional cost to burn mixture over fuel oil, \$/hr | Amount of NC consumed, metric tons/yr |
|----------------------|---|-----------------------------|-----------------------------------|--|---------------------------------------|
| 20                   | 1377 (3)                                | 306                         | 107                               | 199  | 323                                   |
| 30                   | 2065 (5)                                | 459                         | 160                               | 299  | 484                                   |
| 40                   | 2754 (7)                                | 612                         | 213                               | 399  | 645                                   |
| 50                   | 3442 (8)                                | 765                         | 267                               | 499  | 807                                   |

<sup>a</sup>See Appendix C for calculations.

<sup>b</sup>Mixture includes No. 2 fuel oil, acetone, and nitrocellulose.

<sup>c</sup>Gpm = gallons per minute.

64.6% acetone-31.2% No. 2 fuel oil-4.2% nitrocellulose mixture instead of No. 2 fuel oil only are \$211/hr, \$317/hr, \$422/hr, and \$528/hr for a 20, 30, 40, and 50 MBtu/hr boiler, respectively. Similarly, for the 64.8% acetone-29.3% No. 2 fuel oil-5.9% nitrocellulose mixture, the additional costs to burn the mixture versus No. 2 fuel oil only are \$199/hr, \$299/hr, \$399/hr, and \$499/hr for a 20, 30, 40, and 50 MBtu/hr boiler, respectively.

The additional costs incurred for burning the acetone-No. 2 fuel oil-nitrocellulose mixtures are a combination of the following:

1. The cost of acetone is approximately \$0.20 per pound higher than No. 2 fuel oil.
2. The heat of combustion for No. 2 fuel oil is approximately 19500 Btu/lb as compared with acetone, 13229 Btu/lb, and nitrocellulose, 4100 Btu/lb. Because we are adding materials to the No. 2 fuel oil with a lower Btu/lb rating than No. 2 fuel oil itself, the heat of combustion for, e.g., the 64.6% acetone-31.2% No. 2 fuel oil-4.2% nitrocellulose mixture is much lower than the heat of combustion for No. 2 fuel oil only. Therefore, a larger quantity of the acetone-No. 2 fuel oil-nitrocellulose mixture is required to feed a particular boiler size in order to produce the energy required to fire that boiler than is the quantity of No. 2 fuel oil required.

Figure 14 shows a cost comparison of burning No. 2 fuel oil versus the two No. 2 fuel oil-acetone-nitrocellulose mixtures discussed above.

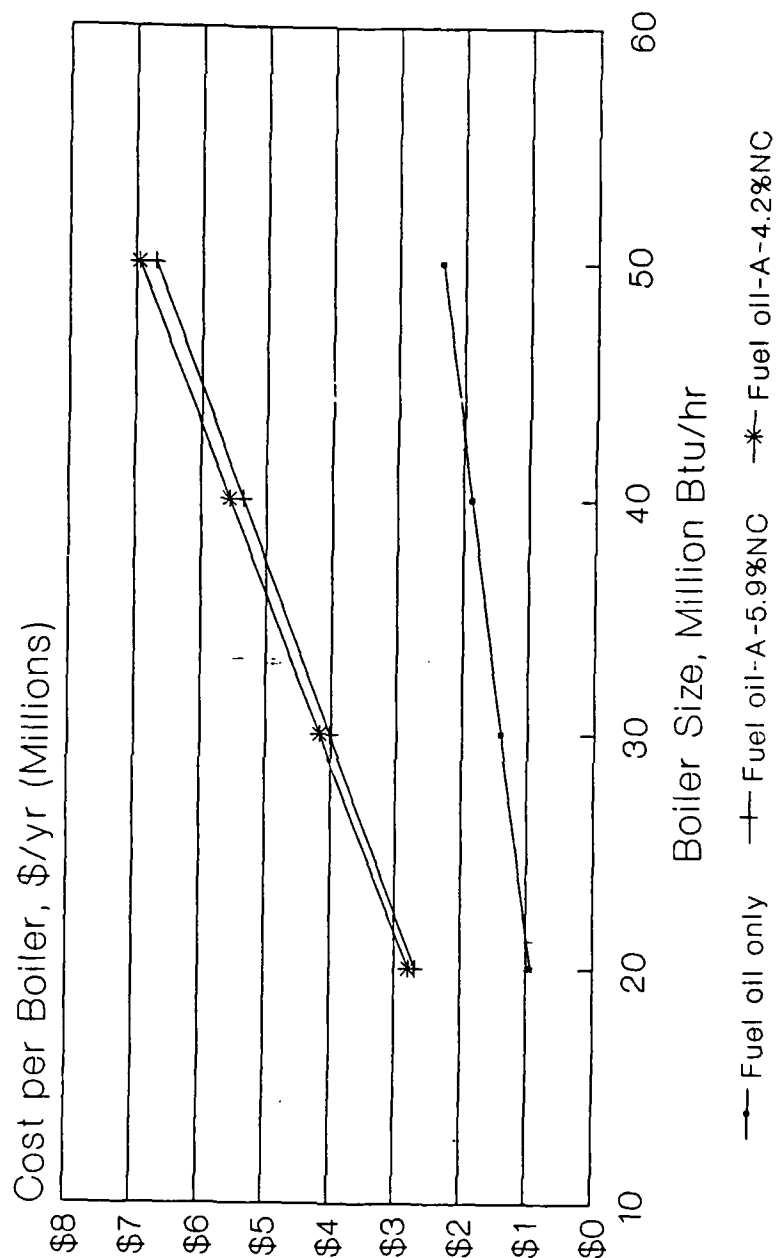
### 3.1.3 Possible Alternatives to Burning Acetone-Nitrocellulose-No. 2 Fuel Oil Mixtures as a Supplemental Fuel

A viable alternative to burning acetone-nitrocellulose-No. 2 fuel oil mixtures as a supplemental fuel might be to suspend the nitrocellulose in No. 2 fuel oil and burn this slurry. Consequently, a preliminary cost comparison for burning a No. 2 fuel oil-nitrocellulose mixture versus No. 2 fuel oil only was performed to substantiate this assumption. As in the previous section, equipment costs were not included in this analysis.

For comparison purposes, arbitrary concentrations of nitrocellulose in the No. 2 fuel oil were chosen between zero and thirty weight percent. The cost to burn the No. 2 fuel oil-nitrocellulose mixtures as a supplemental fuel were then calculated for 20, 30, 40, and 50 MBtu/hr boiler sizes. These cost comparisons are summarized in Table 13. Addition of nitrocellulose to the No. 2 fuel oil decreases the cost to fuel a particular size boiler compared to the cost to fuel the boiler with No. 2 fuel oil only (Figure 15).

Specifically, considering a 20 MBtu/hr boiler, burning a mixture of 5%, 10%, 20%, or 30% nitrocellulose in No. 2 fuel oil instead of No. 2 fuel oil only yields a cost savings of \$31/hr, \$65/hr, \$142/hr, or \$235/hr, respectively. It is also important to note here that if, for

# **FUEL OIL-ACETONE(A)-NITROCELLULOSE(NC)** 4.2% NC AND 5.9% NC (by weight)



USATHAMA (PROJECT RI6)  
TVA CONTRACT NO. 79416

Figure 14. Costs to Burn No. 2 Fuel Oil-Acetone-Nitrocellulose Mixtures in Various Boiler Sizes.



Table 13. Comparison Between Burning No. 2 Fuel Oil Versus  
No. 2 Fuel Oil Containing Nitrocellulose (NC)<sup>a</sup>

| Fraction<br>consumed,<br>of NC<br>(wt. %) | Fraction<br>of<br>fuel<br>oil<br>(wt. %) | Heat of<br>combustion<br>for the<br>mixture,<br>Btu/lb | Mixture<br>input,<br>lb/hr<br>(gpm) <sup>b</sup> | Cost to<br>burn<br>mixture<br>\$/hr <sup>c</sup> | Additional<br>cost to<br>burn mixture<br>over fuel<br>oil, \$/hr <sup>c</sup> | Amount<br>of NC<br>metric<br>tons/yr |
|---|--|--|--|--|---|--------------------------------------|
|---|--|--|--|--|---|--------------------------------------|

BASIS: Boiler Size = 20 MBtu/hr

|      |      |       |          |      |      |      |
|------|------|-------|----------|------|------|------|
| 0.00 | 1.00 | 19500 | 1026 (2) | 107  | ---- | 0    |
| 0.05 | 0.95 | 18730 | 1068 (2) | 76   | -31  | 212  |
| 0.10 | 0.90 | 17960 | 1114 (2) | 42   | -65  | 442  |
| 0.20 | 0.80 | 16420 | 1218 (3) | -35  | -142 | 968  |
| 0.30 | 0.70 | 14880 | 1344 (3) | -128 | -235 | 1602 |

BASIS: Boiler Size = 30 MBtu/hr

|      |      |       |          |      |      |      |
|------|------|-------|----------|------|------|------|
| 0.00 | 1.00 | 19500 | 1538 (4) | 160  | ---- | 0    |
| 0.05 | 0.95 | 18730 | 1602 (4) | 113  | -47  | 318  |
| 0.10 | 0.90 | 17960 | 1679 (4) | 63   | -97  | 664  |
| 0.20 | 0.80 | 16420 | 1827 (4) | -53  | -213 | 1452 |
| 0.30 | 0.70 | 14880 | 2016 (4) | -192 | -352 | 2403 |

BASIS: Boiler Size = 40 MBtu/hr

|      |      |       |          |      |      |      |
|------|------|-------|----------|------|------|------|
| 0.00 | 1.00 | 19500 | 2051 (5) | 213  | ---- | 0    |
| 0.05 | 0.95 | 18730 | 2136 (5) | 151  | -62  | 424  |
| 0.10 | 0.90 | 17960 | 2227 (5) | 84   | -130 | 885  |
| 0.20 | 0.80 | 16420 | 2436 (5) | -70  | -283 | 1936 |
| 0.30 | 0.70 | 14880 | 2688 (5) | -256 | -469 | 3204 |

BASIS: Boiler Size = 50 MBtu/hr

|      |      |       |          |      |      |      |
|------|------|-------|----------|------|------|------|
| 0.00 | 1.00 | 19500 | 2564 (6) | 267  | ---- | 0    |
| 0.05 | 0.95 | 18730 | 2670 (6) | 189  | -78  | 530  |
| 0.10 | 0.90 | 17960 | 2784 (6) | 105  | -162 | 1106 |
| 0.20 | 0.80 | 16420 | 3045 (6) | -88  | -354 | 2420 |
| 0.30 | 0.70 | 14880 | 3360 (7) | -320 | -587 | 4005 |

<sup>a</sup>See Appendix D for calculations.

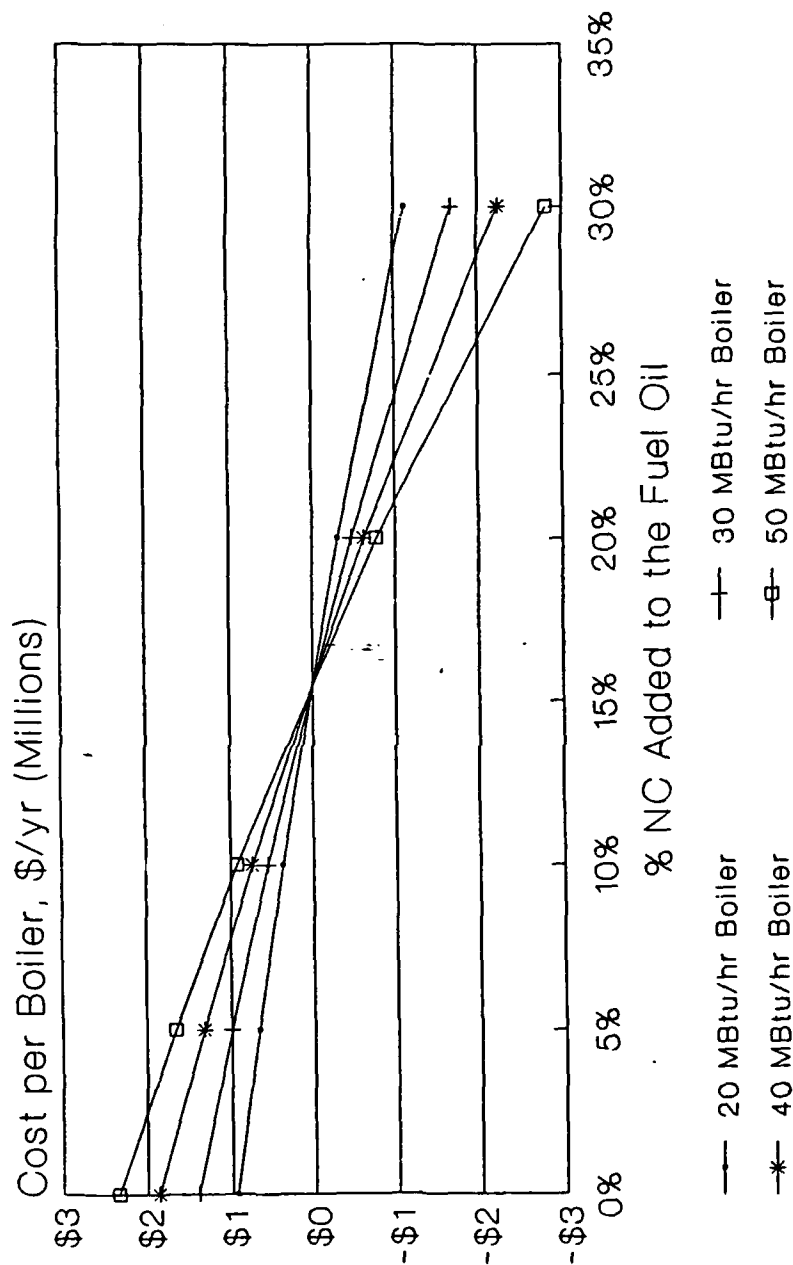
<sup>b</sup>Gpm = gallons per minute.

<sup>c</sup>Negative numbers represent savings.

example, a 30% nitrocellulose-70% No. 2 fuel oil mixture were used to fire a 20 MBtu/hr boiler, approximately 1602 metric tons per year of nitrocellulose could be disposed of.

Furthermore, if the boiler size is increased to 50 MBtu/hr, burning mixtures of 5%, 10%, 20%, or 30% nitrocellulose in No. 2 fuel oil compared to No. 2 fuel oil alone increases the cost savings to \$78/hr, \$162/hr, \$354/hr, or \$587/hr, respectively. As in the previous example, these savings are mainly based on the cost savings from not having to store and incinerate the nitrocellulose. More importantly, burning a 30% nitrocellulose-70% No. 2 fuel oil slurry in a 50 MBtu/hr boiler would dispose of approximately 4005 metric tons of nitrocellulose per year.

# FUEL OIL - NITROCELLULOSE (NC)



USATHAMA (PROJECT RI6)  
TVA CONTRACT NO. 79416

Figure 15. Costs to Burn No. 2 Fuel Oil-Nitrocellulose Mixtures in Various Boiler Sizes.

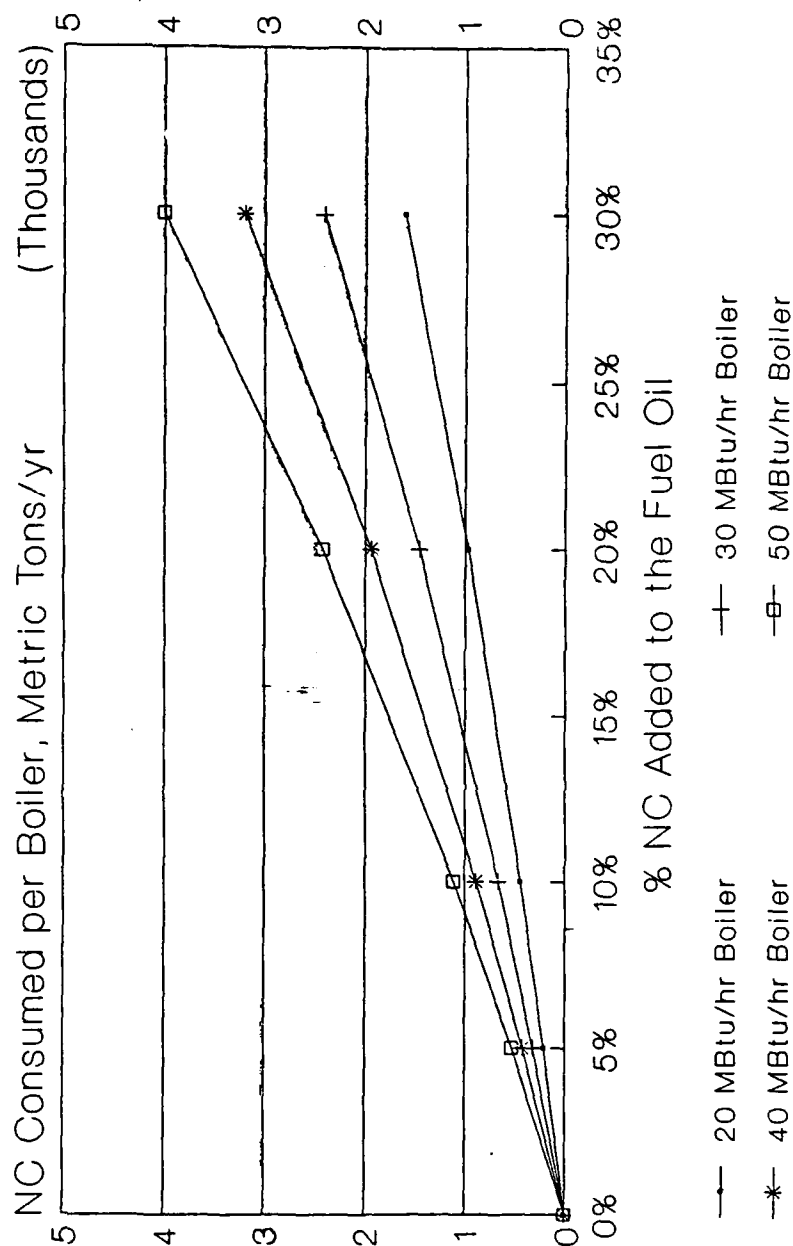
Figure 16 shows the amount of nitrocellulose that could be consumed per year for burning a No. 2 fuel oil-nitrocellulose mixture in each particular boiler size at four different weight percent concentrations of nitrocellulose.

Recall that one of the main drawbacks of using an acetone-nitrocellulose-No. 2 fuel oil solution as a supplemental fuel to fire a boiler was that only a small amount of nitrocellulose (approximately 2% by weight) could be incorporated into the solution without the viscosity rising above the maximum value which could be handled by an unmodified oil burner. Obviously, burning this type of mixture in a boiler, besides being prohibitively expensive, would only dispose of a very small amount of nitrocellulose per year. Considering the large inventory of waste and out-of-specification nitrocellulose-containing propellant in the military's disposal inventory, the alternative process described above becomes worthy of serious consideration.

#### 3.1.4 Conclusions

Based on the various cost comparisons which have been discussed in this analysis, we conclude that fueling boilers with supplemental fuels composed of No. 2 fuel oil-acetone-nitrocellulose mixtures is not a cost-effective process to be recommended for further study at this time. If the price of No. 2 fuel oil increased drastically in the future, this conclusion would need to be reevaluated.

# FUEL OIL - NITROCELLULOSE (NC)



USATHAMA (PROJECT R16)  
TVA CONTRACT NO. 79416

Figure 16. Amounts of Nitrocellulose Consumed per Year for Burning No. 2 Fuel Oil-Nitrocellulose Mixtures in Various Boiler Sizes.

On the other hand, an alternative process where a nitrocellulose-containing propellant would be suspended in No. 2 fuel oil and used as a supplemental fuel for Army industrial combustors does look promising based on the preliminary cost comparisons. Tests to determine the amount of nitrocellulose that could be suspended in No. 2 fuel oil to provide a supplemental fuel with the optimum physical and chemical characteristics for use with conventional oil burner technology need to be conducted and are recommended as the next phase of experiments in this project.

#### 4. EXPERIMENTAL PROCEDURES

The following sections describe the test plan, selection of test materials, preparation of solvent-nitrocellulose and No. 2 fuel oil-solvent-nitrocellulose solutions, and the test methodologies to determine the physical and chemical characteristics, as well as the chemical compatability, of these solutions.

##### 4.1 OVERALL TEST PLAN AND PROCEDURES

Propellants that require disposal by the U.S. Army primarily consist of single-, double-, and triple-base propellants. For a single-base propellant, 85-98% of the composition consists of nitrocellulose; for a double-base propellant, the fraction of nitrocellulose decreases to 55-78%, while for a triple-base propellant, only about 20-28% of the composition consists of nitrocellulose. To determine whether using these nitrocellulose-containing propellants as a supplemental fuel in an industrial combustor was feasible, a series of tests were developed to assess the physical and chemical characteristics, as well as the chemical compatability of a smokeless-grade nitrocellulose (13.15% nitrogen) dissolved in various solvents and further mixed with No. 2 fuel oil.

The smokeless-grade nitrocellulose was used as a substitute for an actual propellant sample for two reasons. First, it was not possible to acquire a sample of actual propellant within the six month time frame of

this project. Second, since nitrocellulose makes up a large fraction of the total composition of single- and double-base propellants, its use as a substitute for the actual propellant was obviously a logical alternative. Based on these reasons, a draft test plan specifying the details of the chemical and physical characteristics tests, as well as the chemical compatibility tests, for solvent-nitrocellulose and No. 2 fuel oil-solvent-nitrocellulose solutions was submitted to USATHAMA for review in November, 1989. After review by USATHAMA's chemistry section, the test plan was approved as a final version at an Interim Project Review meeting held between TVA and USATHAMA personnel at the Edgewood Arsenal in December, 1989.

#### 4.1.1 Selection of Test Sample Materials

##### 4.1.1.1 Nitrocellulose

The smokeless-grade nitrocellulose (Grade C, Type 1, 13.15% nitrogen) was purchased from Hercules Incorporated. Hercules Incorporated supplies nitrocelluloses prepared exclusively from woodpulp. As received, the smokeless-grade nitrocellulose contained at least 20% by weight water. Nitrocellulose is always wet with water or alcohol in commercial handling, shipping, and storage, in which condition it presents no unusual hazard.



#### 4.1.1.2 Solvent Components

Analytical grades of acetone, ethyl acetate, butyl acetate, 2-butanone, tetrahydrofuran, and toluene were purchased from a commercial vendor (VWR Scientific) and used without further purification.

#### 4.1.1.3 Fuel Oil Component

A commercial grade of No. 2 fuel oil was purchased from a local distributor. A typical analysis of this oil is shown in Table 14.

Table 14. Analysis of Commercial No. 2 Fuel Oil

| <hr/>                                  |                     |
|--|---------------------|
|  | <u>Grade number</u> |
|  | 2                   |
| <hr/>                                  |                     |
| <u>Element</u>                         |                     |
| Carbon, %                              | 86.35               |
| Hydrogen, %                            | 12.72               |
| Oxygen, %                              | 0.82                |
| Nitrogen, %                            | <0.01               |
| Sulfur, %                              | 0.10                |
| Ash, %                                 | 0.01                |
| Density, lb/gal at 16°C (60°C)         | 7.208               |
| Heat of Combustion, Btu/lb             | 19,500              |
| Viscosity, centistokes at 38°C (100°F) | 3.7                 |
| <hr/>                                  |                     |

#### 4.1.2 Mix Preparation

##### 4.1.2.1 Drying of Nitrocellulose

Nitrocellulose (20 g) containing 20-30% of moisture was dried for 16 h at 60°C and then 5 g portions were placed in weighing bottles and dried at 100°C until a constant weight was obtained. The oven used for drying the nitrocellulose had the latch removed for safety reasons. A face mask was worn when the oven was opened after the samples had been heated. Dry nitrocellulose, if ignited by fire, spark, or static electricity, burns very rapidly. Consequently, only enough nitrocellulose required to perform a particular test was dried. Any nitrocellulose left over after a particular test was wet with water and disposed of properly.

##### 4.1.2.2 Preparation of Nitrocellulose-Solvent Mixtures

The appropriate amount of nitrocellulose was weighed out on an analytical balance to the nearest 0.01 g and transferred to a stoppered, preweighed 125-ml Erlenmeyer flask. The balance was tared, and the appropriate amount of solvent was added and this weight recorded also. Parafilm was placed around the stopper to seal the flask and prevent any solvent vapors from escaping. The flask was then placed on a Lab-Line Orbit Environ-Shaker and swirled for 24 h at a setting of 200 rpm and a temperature of  $21 \pm 1^\circ\text{C}$ .

#### 4.1.2.3 Preparation of Nitrocellulose-Solvent-No. 2 Fuel Oil Mixtures

The appropriate amount of nitrocellulose was weighed out on an analytical balance to the nearest 0.01 g and transferred to a preweighed 8 oz. glass bottle (Baxter Scientific Products). The balance was tared, and the appropriate amount of solvent was added and this weight recorded also. The lid was screwed onto the bottle, and the bottle was placed on a Eberbach Corp. reciprocating shaker for 24 h at low speed and ambient temperature. A predetermined amount of No. 2 fuel oil (based on the values of the dilution ratio measured for each specific nitrocellulose-solvent mixture (Table 1) minus 10-30% to make sure that precipitation did not occur) was then added in 3-5 ml portions, with the mixture being placed back on the shaker at low speed after each addition until the No. 2 fuel oil became completely blended into the nitrocellulose-solvent solution. The resulting nitrocellulose-solvent-No. 2 fuel oil mixture was then either immediately used for a test or was left on the shaker until needed.

### 4.2 PHYSICAL CHARACTERISTICS TESTS

#### 4.2.1 Solubility Tests

Initially, the miscibility of potential solvents for nitrocellulose in the No. 2 fuel oil was determined according to the standard procedure given below. The potential solvents investigated were acetone, ethyl

acetate, tetrahydrofuran, 2-butanone, butyl acetate, and toluene. Each potential solvent was found to be completely miscible with the No. 2 fuel oil at room temperature.

#### 4.2.1.1 Solubility of Liquids in Liquids at Constant Temperature

This method of determining the solubility of liquids in liquids at constant temperature is based on measuring the volume changes of two liquid phases as they equilibrate with each other, and can be applied to any liquids that might separate to form a sharp interface after mixing. Graduated cylinders, burets, or specially constructed flasks are used during this experiment.

In general, two separate mixtures of the two liquids  $L_1$  and  $L_2$  are prepared, and the original weight of each liquid is measured. In the first mixture, a large amount of liquid  $L_1$  is used with a small amount of  $L_2$ , and in the second mixture it is the reverse--a large amount of  $L_2$  with a small amount of  $L_1$ . Each mixture is then thoroughly mixed and allowed to separate. If the mixtures separate to form a sharp interface after mixing, then the volumes of the top and bottom layers are read ( $V_1$ ,  $V_3$  and  $V_2$ ,  $V_4$ , respectively).

Even though the relative proportions of the upper and lower layers differ, the compositions of the upper and lower layers in the two mixtures are the same because the solubility of each liquid in the other

is a constant at a given temperature. The total (original) amount of each liquid is now distributed between the two layers, and if

$\underline{x}$  = concentration (g/ml) of  $L_1$  in the upper layer, and

$\underline{y}$  = concentration (g/ml) of  $L_1$  in the lower layer

then

Total wt.  $L_1$  in the first mixture =  $\underline{x}V_1 + \underline{y}V_2$

Similarly:

Total wt.  $L_1$  in the second mixture =  $\underline{x}V_3 + \underline{y}V_4$

These equations are then solved simultaneously for  $\underline{x}$  and  $\underline{y}$ . If the densities of the equilibrium upper and lower layers are also determined, the concentrations (grams per milliliter) can be converted to a strictly weight basis.

#### 4.2.1.2 Solubility of Solids in Liquids

For the variable-composition method<sup>18,19</sup> of determining the solubility of a crystalline solid in a liquid, the general procedure is

to prepare a saturated solution at equilibrium with the undissolved solute, remove a sample of the solution, and subject it to a suitable analysis.

The chief problem which must be solved when using this method is that of obtaining a sample which truly reflects the equilibrium situation. In particular, the applicability of any given sampling technique must be judged in relation to the nature of the system to be sampled (i.e., viscosity, relative stability of the solution constituents, etc.) and to the conditions under which the equilibrium to be studied exists (i.e., unusual conditions of temperature, pressure, etc.).

Direct filtration is the method most widely used for separations of phases in solubility studies. Since the chief requirement upon the filter itself is that of efficient filtration (i.e., pore fineness), as well as inertness toward the system under study, a great variety of filtering media are available, the choice depending mainly upon the nature of the system. The best filter medium identified during this project for the removal of colloidal-type solids was a fine-pore fritted glass funnel, with the filtration being accomplished under mild pressure.

In general, after a sample of the saturated system has been obtained, the simplest and most straightforward method of determining the amount of solute dissolved in the solvent at saturation is to evaporate a weighed sample of the solution to dryness and to determine by weight the solid

residue remaining. When this method is employed, it is usually advisable to keep the evaporation temperature at the lowest practical level and, particularly when the solute is an organic material, it is advisable to carry out the operation at room temperature, using a fan to aid the evaporation.

This general procedure was initially tried with mixtures of nitrocellulose and the five candidate solvents. The solubility apparatus used in these experiments to try and prepare an equilibrium solution was invented at TVA-NFERC<sup>20</sup>. Unfortunately, we found that it was not possible to obtain a definitive quantitative value for the "solubility" of nitrocellulose in the five candidate solvents. This is due to the fact that nitrocellulose is a polymeric material, and as discussed in a previous section (item 2.1.1.2), high polymers show a behavior toward solvents quite different from that of substances with smaller molecular weights and crystalline structures. Some, notably chain polymers, swell continuously in certain solvents until finally a homogeneous solution is formed. There is no saturation equilibrium and no numerical value of solubility. Rather, at a given temperature, liquids may be classed sharply as solvents or nonsolvents for the particular polymer. Thus, for the smokeless-grade nitrocellulose used in this project, acetone, tetrahydrofuran, 2-butanone, ethyl acetate, and butyl acetate may be classified as solvents, while toluene and No. 2 fuel oil are classified as nonsolvents.

#### 4.2.2 Dilution Ratio Experiments

American Society for Testing Materials (ASTM) standard procedure D1720-88, "Standard Test Method for Dilution Ratio of Active Solvents in Cellulose Nitrate Solutions", defines a dilution ratio as the maximum number of unit volumes of a diluent (nonsolvent) that can be added to a unit volume of solvent to cause the first persistent heterogeneity (precipitation) in a solution of nitrocellulose at a concentration of 8 g cellulose nitrate per 100 ml of combined solvent plus diluent at a temperature of  $25 \pm 3^\circ\text{C}$  (Appendix A). During preliminary dilution ratio tests, we found that a concentration of 8 g nitrocellulose per 100 ml of combined solvent plus diluent could not be attained using the 13.15% nitrogen content, smokeless-grade nitrocellulose used in this project. Specifically, the nitrocellulose-solvent mixtures became extremely viscous and could not be swirled after the No. 2 fuel oil diluent was added. Consequently, a slightly modified procedure had to be used to successfully perform the dilution ratio experiments. However, this modified procedure still provided the required information concerning the amount of No. 2 fuel oil which could be added to various concentrations of smokeless-grade nitrocellulose in each candidate solvent before precipitation of the nitrocellulose occurred.

Specific examples for each of the five candidate solvents will now be discussed. First, for the dilution ratio tests with the nitrocellulose-acetone mixtures, concentrations of 1.4, 3.7, 6.0, and



8.3% by weight nitrocellulose in acetone were prepared. Second, for the dilution ratio tests with the nitrocellulose-ethyl acetate mixtures, concentrations of 1.2, 3.3, 5.3, and 7.3% by weight nitrocellulose in ethyl acetate were initially prepared, however, the solution containing 7.3% nitrocellulose was too viscous to effectively perform the dilution ratio test (i.e., this solution could not be swirled in the flask). Third, for the dilution ratio tests with the nitrocellulose-tetrahydrofuran mixtures, concentrations of 1.2, 3.3, 5.4, and 7.3% by weight nitrocellulose in tetrahydrofuran were initially prepared, however, once again the solution containing 7.3% nitrocellulose was too viscous to effectively perform the test. Fourth, for the dilution ratio test with the nitrocellulose-butyl acetate mixtures, concentrations of 1.4, 2.8, 4.1, and 5.4% by weight nitrocellulose were prepared, but the solution containing 5.4% nitrocellulose was too thick to effectively perform the dilution ratio test. Fifth, for the dilution ratio test with the nitrocellulose-2-butanone mixtures, concentrations of 1.4, 3.7, 5.9, and 7.0% by weight nitrocellulose in 2-butanone were prepared. The solution containing 7.0% nitrocellulose in 2-butanone was too viscous to effectively perform the dilution ratio test.

The No. 2 fuel oil diluent, maintained at  $25 \pm 3.0^{\circ}\text{C}$ , was added to the flask from a 50 ml buret in small additions. Five-milliliter increments were added at first, but this was decreased to about 0.5-1.0 ml increments as the end point was approached. After each addition, the flask was stoppered and swirled vigorously to disperse any gel or

precipitate thrown down by local overconcentration of No. 2 fuel oil diluent. As was particularly the case with acetone, tetrahydrofuran, and 2-butanone, special care was taken to prevent loss of these volatile solvents by evaporation. When precipitation persisted after at least 2 min of vigorous swirling, the initial end point was reached, as indicated by the presence of gel particles in the solution or on the sides of the flask. Acetone, ethyl acetate, 2-butanone, and butyl acetate each gave an end point where gel particles were observed either in solution or on the sides of the flask, while tetrahydrofuran gave a cloudy end point with no indication of gel particles formed in the solution. In each case, the total volume of No. 2 fuel oil diluent added to the flask at this point was recorded.

A second end point was then determined using the same solution. First additional solvent was titrated into the flask to redissolve the nitrocellulose which had precipitated from solution. The amount of solvent added depended on the amount of No. 2 fuel oil diluent used in the initial titration, but was generally in the range of 1.0-3.0 ml. After addition of the required amount of solvent, the flask was swirled to redisperse the nitrocellulose. Then, the titration was continued with No. 2 fuel oil diluent to the second end point using 0.5 ml increment additions of diluent. Lastly, the total volume of No. 2 fuel oil diluent added to the flask at this point was recorded.

#### 4.2.3 Viscosity Tests

##### 4.2.3.1 Falling Ball Viscometer

The viscosities of the various nitrocellulose-solvent and nitrocellulose-solvent-No. 2 fuel oil mixtures were measured at 20 and 50°C using a falling-ball viscometer by closely following the standard procedure outlined in ASTM standard procedure D1343-86 (Appendix A). A diagram of the falling ball viscometer<sup>21</sup> is shown in Figure 16. The viscometer as received from the manufacturer was supplied with a glass ball and a stainless steel ball. After reading the instructions supplied by the manufacturer, a tantalum ball was also ordered which increases the range of each viscometer size. The recommended ranges of viscosity for each viscometer size and type of ball are as given in Table 15.

Table 15. Falling Ball Viscometer Sizes and Viscosity Ranges

| <u>Size No.</u> | <u>Range in centipoise</u> |                 |             |
|-----------------|----------------------------|-----------------|-------------|
|                 | Glass                      | Stainless Steel | Tantalum    |
| 1               | 0.2 to 2                   | 1 to 10         | 2 to 20     |
| 2               | 2 to 20                    | 10 to 100       | 20 to 200   |
| 3               | 20 to 200                  | 100 to 1000     | 200 to 2000 |

The instrument full of liquid (approximately 5 ml) was inverted until the ball entered the Teflon screw, and then the knob was turned until the closed position was reached (see Figure 17). The instrument was then restored to its normal vertical position and immersed in a constant temperature bath. The ball was released by turning the knob to raise the Teflon screw. The time of descent between the two sets of fiduciary lines was measured with a stopwatch. Repeat measurements were made by removing the viscometer from the constant temperature bath, inverting it to return the ball to the screw, and then turning the Teflon screw to the closed position. At least three sets of measurements were made for each nitrocellulose-solvent or nitrocellulose-solvent-No. 2 fuel oil mixture at each temperature.

For a falling ball viscometer, the viscosity is calculated by a simple formula:

$$V = K(p_f - p)t$$

where  $V$  = viscosity in centipoises  
 $p_f$  = density of ball (g/ml)  
2.53 for glass  
8.02 for stainless steel  
16.6 for tantalum  
 $p$  = density of liquid (g/ml)  
 $t$  = time of descent (min)  
 $K$  = viscometer constant

The viscometer constant is obtained by measuring the time of descent for each type of ball in a standard liquid at each temperature:

$$K = \frac{V}{(p_f - p)t}$$

Specifically, the viscometer tube size #1 was calibrated with distilled water, while a glycerol-water mixture (95% glycerol) was used for the viscometer tube sizes # 2 and 3. The calibration constants are summarized in Table 16.

OVERALL SIZE  
10" LONG x 1" DIA.

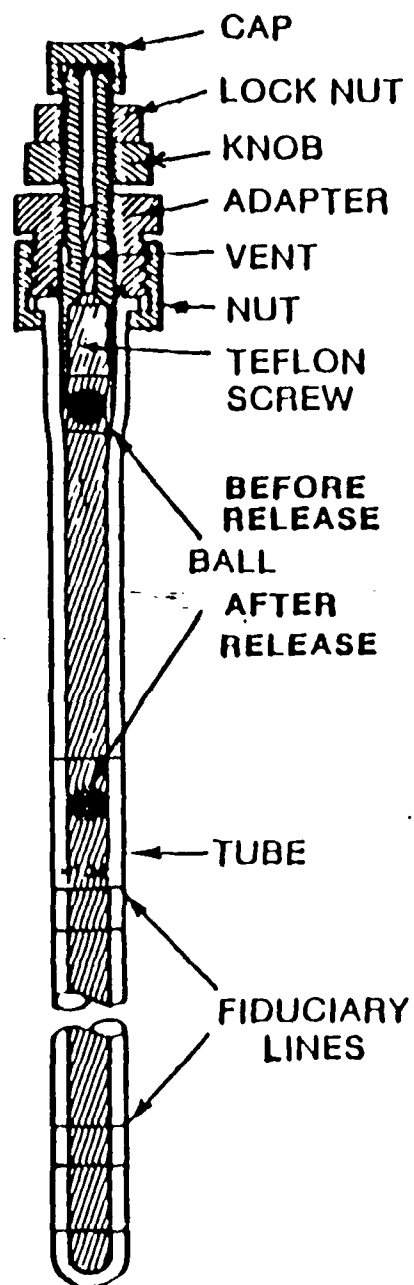


Figure 17. Diagram of a Falling Ball Viscometer.

Table 16. Calibration Constants for Each Falling Ball Viscometer

| <u>Size No.</u> | <u>Glass</u> |       | <u>Stainless Steel</u> |       | <u>Tantalum</u> |       |
|-----------------|--------------|-------|------------------------|-------|-----------------|-------|
|                 | 20°C         | 50°C  | 20°C                   | 50°C  | 20°C            | 50°C  |
| 1               | 0.214        | 0.200 | 0.197                  | 0.162 | ---             | ---   |
| 2               | ---          | ---   | 3.711                  | 2.680 | ---             | ---   |
| 3               | ---          | ---   | 28.60                  | 27.23 | 70.11           | 41.26 |

#### 4.2.3.2 Brookfield Viscometer

A much larger volume of nitrocellulose-containing solution was required for viscosity tests with the Brookfield digital viscometer (Model DV-II), consequently, measurements were taken with this instrument only on nitrocellulose-solvent mixtures at 25°C. These tests were performed according to ASTM D 2196-86 standard procedure (Appendix A). This procedure covers the determination of the apparent viscosity, as well as the shear thinning and thixotropic properties of non-Newtonian materials in the shear rate range from 0.1 to 50 s<sup>-1</sup>.

Two standard oils of viscosities differing by at least 50 centipoise were used to calibrate the viscometer. Various nitrocellulose-solvent mixtures (300 ml volumes) were prepared in 16 oz. glass bottles. These mixtures were conditioned prior to each measurement by shaking on a reciprocating shaker for 10 min, removed from the shaker, and allowed to stand undisturbed for 60 min at 25°C. The nitrocellulose-solvent mixtures were then measured at various spindle/speed combinations to assess how the viscosity changes under changing speed conditions.

#### 4.2.4 Density Tests

Density measurements were performed with a glass hydrometer on nitrocellulose-solvent and nitrocellulose-solvent-No. 2 fuel oil solutions at 20 and 50°C according to ASTM D1298-85 standard procedure (Appendix A). The hydrometer method is most suitable for determining the density of mobile transparent liquids. However, it can also be used for viscous oils by allowing sufficient time for the hydrometer to reach equilibrium.

The sample of nitrocellulose-solvent or nitrocellulose-solvent-No. 2 fuel oil solution was equilibrated at 20 or 50°C and transferred to a hydrometer cylinder at approximately the same temperature. The appropriate hydrometer was then lowered into the sample. Particularly in the case of the more viscous samples, sufficient time was allowed for the hydrometer to come to rest and for all the air bubbles entrained in the sample to come to the surface. After temperature equilibrium was reached, the hydrometer scale was read, and the temperature of the sample was measured. In each case, the hydrometer cylinder and its contents were placed in a constant temperature bath to avoid excessive temperature variation during the test.

In some cases, particularly with the more viscous samples, the density value obtained with the hydrometer was confirmed by measuring the density according to the procedure given in ASTM D1343-86 standard



procedure. In this procedure, the density of the sample in grams per cubic centimeter is determined by measuring the volume at 20 or 50°C of a known weight of the sample contained in a 25 ml tightly stoppered graduated cylinder. In all cases, the density value determined with either method agreed to within 0.002 grams per cubic centimeter.

#### 4.3 CHEMICAL CHARACTERISTICS TESTS

##### 4.3.1 Flash Point Tests

The flash points of solvent-No. 2 fuel oil and solvent-No. 2 fuel oil-nitrocellulose mixtures were determined using the Pensky-Martens closed-cup tester according to ASTM D93-85 standard procedure (Appendix A). In this test, the sample is heated at a slow, constant rate with continual stirring. A small flame is directed into the cup at regular intervals with simultaneous interruption of stirring. The flash point is defined as the lowest temperature at which application of the test flame causes the vapor above the sample to ignite. Several of the solvent-No. 2 fuel oil and solvent-No. 2 fuel oil-nitrocellulose mixtures had to be cooled in a dry ice-acetone bath prior to the determination of their flash points. In addition, extreme care was exercised during this test to prevent backflash of the flame into the solvent, which might easily have resulted in explosive decomposition of the nitrocellulose-containing solutions.

#### 4.3.2 Fire Point Tests

The fire points of solvent-No. 2 fuel oil and solvent-No. 2 fuel oil-nitrocellulose mixtures were determined using a Cleveland Open-Cup apparatus according to ASTM D92-85 standard procedure (Appendix A). In this test, the specimen is placed in the cup of a Cleveland Open-Cup apparatus and heated rapidly at first but then at a slow, constant rate as the flash point is approached. A small test flame is passed at a uniform rate across the cup at specified intervals until application of the test flame causes the specimen to burn for at least 5 seconds. Again, several of the solvent-No. 2 fuel oil and solvent-No. 2 fuel oil-nitrocellulose mixtures had to be cooled in a dry ice-acetone bath prior to the determination of their fire points. It was originally anticipated that this test might only be applicable to the solvent-No. 2 fuel oil mixtures, without any nitrocellulose, because it seemed likely that an explosion would occur if the solvent-No. 2 fuel oil-nitrocellulose mixtures were ignited and allowed to burn for 5 seconds. However, preliminary tests on these samples where a small amount was placed in a metal cup and ignited showed that the solvent-No. 2 fuel oil-nitrocellulose samples burned in a similar manner to the solvent-No. 2 fuel oil samples.

#### 4.3.3 Heat of Combustion Tests

The heat of combustion of the smokeless-grade nitrocellulose, No. 2 fuel oil, solvents, and nitrocellulose-solvent-No. 2 fuel oil mixtures were measured using a bomb calorimeter according to ASTM D240-87 standard procedure (Appendix A). The heat of combustion is a measure of the energy available from a fuel. A knowledge of this value is essential when considering the thermal efficiency of equipment for producing either power or heat.

The heat of combustion values for each sample were determined in this test method by burning a weighed sample of material in an oxygen bomb calorimeter under controlled conditions. The heat of combustion was computed from temperature observations before, during, and after combustion, with proper allowance for thermochemical and heat transfer corrections. These tests were performed by the Tennessee Valley Authority's analytical laboratories in Chattanooga, Tennessee.

### 4.4 CHEMICAL COMPATABILITY TESTS

#### 4.4.1 Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) is a technique in which the difference in energy inputs into a substance and a reference material is measured as a function of temperature while the substance and reference

material are subjected to a controlled temperature program. This technique is useful for detecting potentially hazardous reactions including those from volatile chemicals and for estimating the temperatures at which these reactions occur. In addition, this technique is recommended as an initial test for detecting the reactive hazards of an uncharacterized chemical substance or mixture.

The DSC experiments were performed according to ASTM E 537-86 standard procedure (Appendix A) using a Perkin-Elmer model DSC-7 instrument. A heating rate of 10°C/min was used in each experiment with a nitrogen flow rate of 65 cc/min. The apparatus was calibrated in temperature and surface area with indium ( $T_m = 156^\circ\text{C}$  and  $H_m = 28.4$  J/g). An empty pan was used as the reference material for all measurements. The surface areas were measured by manipulating the decomposition curves and baselines with the DSC-7 computer software.

The method for crimping the pans was identical to that discussed by Lemieux et al.<sup>22</sup>. First, the sample (0.5-1.5 mg) was crimped in the usual manner with aluminum pan and cover. Then, the rim of the capsule was pinched with tweezers in a criss-cross way so that decomposition gases could escape easily. This operation leaves the bottom of the capsule uniform to allow a proper thermal contact between the sample holder and the capsule. The sample was then placed in the DSC-7 apparatus, brought rapidly to 117°C, and equilibrated for two minutes. The DSC experiment was then performed at a heating rate of 10°C/min, from

117 to 277°C, under a nitrogen flow rate of 65 cc/min. Finally, after reaching 277°C, the instrument was rapidly cooled to 117°C and the equilibrium and heating cycle was repeated in order to draw the sample baseline.

#### 4.4.2 Supplementary Tests

Qualitative analyses of nitrocellulose-solvent, nitrocellulose-solvent-No. 2 fuel oil, and solvent-No. 2 fuel oil mixtures were conducted over the six month course of this project to determine, for example, if any color changes, separation of phases, or precipitation occurred. Specific results from these observations are discussed in sections 2.3.2.1 and 2.3.2.2.

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## 6. LITERATURE SEARCH

### 6.1 Literature Sources

Previous work in the scientific literature concerning the solubility, solution chemistry, physical characteristics, chemical characteristics, and thermal stability of nitrocellulose with various weight percent nitrogen contents and nitrocellulose-based materials in various solvents were identified using the STN computer database. This database does not provide references published prior to 1964. Therefore, the Chemical Abstracts reference database was searched manually by TVA personnel for pertinent literature articles published prior to 1964.

### 6.2 Search Strategy

A total of 587 references were obtained from the STN computer database using the following search keywords: Nitrocellulose, Cellulose Nitrate, Solubility, Solubilities, Reactions, Chemistry, Decomposition, and Physical Properties. Copies of pertinent literature articles, reports, and patents were obtained and the full contents of each article was reviewed for relevance to the current project. A full listing of all literature articles obtained in both the STN computer and Chemical Abstracts literature searches is given in Appendix B. A copy of the original computer printout from the STN database literature search is available from the authors upon request. Also available from the authors



upon request are copies of any of the articles, patents, or government reports listed in Appendix B.

Reference material gathered in the literature search included previous work that USATHAMA has sponsored, including, but not limited to: (1) the chemical stability and reactivity of supplemental fuels consisting of a mixture of fuel oil and explosives, and (2) waste propellant reuse and recovery technology.

**APPENDIX A**  
**ASTM STANDARD PROCEDURES**

ASTM D 1720-88

Standard Test Method for Dilution Ratio of  
Active Solvents in Cellulose Nitrate Solutions



Designation: D 1720 - 88

## Standard Test Method for Dilution Ratio of Active Solvents in Cellulose Nitrate Solutions<sup>1</sup>

This standard is issued under the fixed designation D 1720; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

*This standard has been approved for use by agencies of the Department of Defense to replace Method 4204.1 of Federal Test Method Standard No. 141. Consult the DoD Index of Specifications and Standards for the specific year of issue which has been adopted by the Department of Defense.*

### 1. Scope

1.1 This test method covers the determination of the volume ratio of hydrocarbon diluent to active solvent required to cause persistent heterogeneity (precipitation) in a solution of cellulose nitrate.

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 the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use. For specific hazard statements, see Section 6.*

1.3 For hazard information and guidance, see the supplier's Material Safety Data Sheet.

### 2. Referenced Documents

#### 2.1 ASTM Standards:

D 301 Methods of Testing Soluble Cellulose Nitrate<sup>2</sup>

D 841 Specification for Nitration Grade Toluene<sup>3</sup>

### 3. Description of Term Specific to This Standard

3.1 *dilution ratio*—the maximum number of unit volumes of a diluent that can be added to a unit volume of solvent to cause the first persistent heterogeneity (precipitation) in the solution at a concentration of 8 g cellulose nitrate per 100 mL of combined solvent plus diluent and at a temperature of  $25 \pm 3^\circ\text{C}$ .

NOTE 1—The dilution ratio decreases as the cellulose nitrate concentration at the end point increases. It is, therefore, necessary to set an arbitrary concentration of cellulose nitrate as part of the dilution ratio term. For this purpose 8.0 g of cellulose nitrate per 100 mL of solvent plus diluent has been adopted.

### 4. Significance and Use

4.1 By use of standard or reference grade materials for any two of the three components, namely, oxygenated solvent, diluent, or cellulose nitrate, the effect of different batches or different types of the third component can be determined.

4.2 This test method is applicable for the determination of the following:

4.2.1 The dilution ratio of toluene as the standard diluent to an oxygenated solvent under test, using as the solute standard cellulose nitrate as defined in 5.2.

4.2.2 The dilution ratio of a hydrocarbon diluent under test to *n*-butyl acetate as the standard solvent, using as a solute standard cellulose nitrate as defined in 5.2.

4.2.3 The dilution ratio of toluene, as the standard diluent, to *n*-butyl acetate as the standard solvent, using as the solute cellulose nitrate of varying solubility characteristics.

### 5. Materials

#### 5.1 *n*-Butyl Acetate (90 to 92 %).

NOTE 2—This grade of *n*-butyl acetate contains 8 to 10 % *n*-butyl alcohol.

5.2 *Cellulose Nitrate*, conforming to the Sampling section (Appearance, Ash, and Stability requirements) of Methods D 301 and of such quality that, when used in determining the toluene dilution ratios of *n*-butyl acetate and methyl *n*-propyl ketone, it will give results between the following limits:

|                                | Toluene Dilution Ratio |
|--------------------------------|------------------------|
| <i>n</i> -butyl acetate        | 2.73 to 2.83           |
| methyl <i>n</i> -propyl ketone | 3.80 to 3.90           |

#### 5.3 *Toluene (Toluol)*, conforming to Specification D 841.

### 6. Hazards

6.1 Soluble cellulose nitrate is a flammable material, the degree of flammability varying with the extent and nature of the wetting medium. Cellulose nitrate is always wet with water or alcohol in commercial handling, shipping, and storage, in which condition it presents no unusual hazard. Dry cellulose nitrate, if ignited by fire, spark, or static electricity, burns very rapidly. Do not store samples of dry cellulose nitrate at any time. Dry only that portion required for immediate test. Wear a face shield when the oven is opened after samples have been heated. Wet excess material and the samples left after testing with water and dispose of properly.

### 7. Drying Cellulose Nitrate

7.1 Dry not more than 20 g of cellulose nitrate at a time by spreading in a thin layer on a tray at room temperature for 12 to 16 h, or on top of a  $100^\circ\text{C}$  oven where the

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee D-1 on Paint and Related Coatings and Materials and is the direct responsibility of Subcommittee D01.35 on Solvents, Plasticizers, and Chemical Intermediates.

Current edition approved March 25, 1988. Published May 1988. Originally published as D 1720 - 60 T. Last previous edition D 1720 - 84.

<sup>2</sup> Annual Book of ASTM Standards, Vol 06.02.

<sup>3</sup> Annual Book of ASTM Standards, Vol 06.03.

temperature is 35 to 40°C for about 8 h (Warning, see 6.1). Alternatively, use a steam or hot water-heated oven maintained at 45 to 50°C to dry specimens in about 8 h. For safety reasons, the oven should have the latch removed.

7.2 Another simple way to dry small quantities of cellulose nitrate is to use a drier assembled from common laboratory apparatus. The assembled drier is shown in Fig. 1. Hot air from a laboratory electric oven is drawn through wet cellulose nitrate contained in a brass tube hooked up through a thistle tube, or small funnel, and suction flask to a water aspirator or other vacuum source. The brass pipe should be about 1½ in. (40 mm) in diameter and 8 in. (200 mm) long, these relative dimensions having been found to give efficient results. Such a tube will hold about 25 g, dry weight, of wet cellulose nitrate. The pipe is insulated to conserve heat. The suction flask end of the brass tube is fitted with a thistle tube, or a small funnel, over the mouth of which is tied a silk cloth screen. An indentation made in the funnel edge allows insertion of the thermometer. The funnel and thermometer are held in place by means of a rubber stopper. When using an oven temperature of 85°C and vacuum supplied by a water aspirator or other vacuum source, the alcohol-wet cellulose nitrate will be dried in about 4 h.

7.3 If larger quantities of cellulose nitrate are required, the drying equipment described in the Procedure section of Drying Samples of Methods D 301 may be used.

## 8. Preparation of Solution

8.1 When testing either a solvent or diluent, first estimate the probable dilution ratio for the unknown component in relation to the other to determine the amount of solvent required to dissolve the cellulose nitrate (Table 1). This volume of solvent should be such that there will be approximately 10 g of cellulose nitrate present per 100 mL of solvent plus diluent at the end point.

NOTE 3—Reference to published data on similar types of solvents or diluents will provide a good approximation of the amount of solvent required. If data are not available, several solutions with varying amounts of solvents may be required to arrive at a suitable volume to use.

8.2 On an analytical balance, weigh  $5 \pm 0.01$  g of the cellulose nitrate into a 125-ml, cork-stoppered, preweighed Erlenmeyer flask, or other suitable container. From a buret add the volume of solvent indicated in Table 1. Swirl the flask until the cellulose nitrate is completely dissolved. When a high concentration of cellulose nitrate in solvent is required, dispersion may be more quickly accomplished by adding a measured portion of the diluent to the flask. This

reduces the solids concentration and thus lowers the viscosity of the solution, making it easier to dissolve the cellulose nitrate.

TABLE 1 Volume of Solvent Required to Dissolve Cellulose Nitrate

| Probable Dilution Ratio, volume of diluent: volume of solvent | mL of Solvent per 5 g of Cellulose Nitrate at 25°C |
|---|--|
| 1   | 25.0   |
| 2   | 16.7   |
| 3   | 12.5   |
| 4   | 10.0   |
| 5   | 8.3  |

## 9. Procedure

9.1 Add the diluent, maintained at  $25 \pm 3.0^\circ\text{C}$ , to the flask from a buret in small additions. Five-millilitre increments may be added at first, but these shall be decreased to about 0.5 mL as the end point is approached. After each addition, stopper the flask and swirl vigorously to disperse any gel or precipitate thrown down by local overconcentration of diluent (Note 4). When precipitation persists after at least 2 min of vigorous swirling, the initial end point has been reached, as indicated by the presence of gel particles in the solution or on the sides of the flask (Note 5). Determine the total volume of diluent added to the flask at this point.

NOTE 4—Take care to prevent loss of volatile components by evaporation. Avoid contact of the solution with the stopper.

NOTE 5—Presence of a uniform fine haze that is usually formed when aliphatic hydrocarbons are used as diluents must not be confused with the gel end point.

9.2 Determine a second end point using the same solution. This requires addition of solvent to redissolve the cellulose nitrate. The amount of solvent to add depends upon the amount of diluent used in the initial titration. The volume of solvent to be added is obtained directly from Fig. 2 and the volume of diluent used to reach the initial end point.

9.3 After addition of the required volume of solvent, swirl the flask to redisperse the cellulose nitrate. Then, continue the titration with diluent to the second end point, at which point there should be approximately 8 g of cellulose nitrate present per 100 mL of solvent plus diluent.

## 10. Calculation

10.1 Calculate the dilution ratio and cellulose nitrate

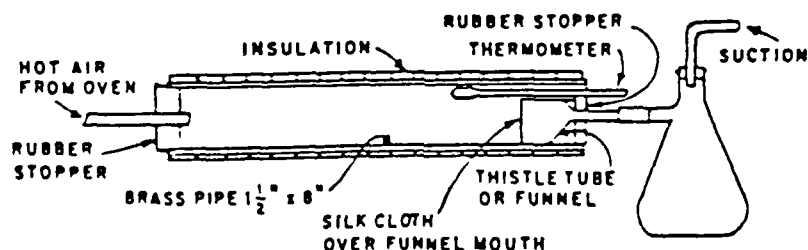


FIG. 1 Assembled Drier

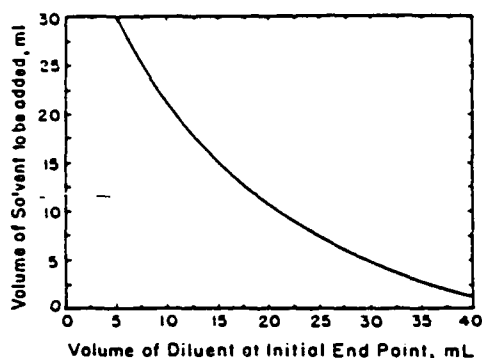


FIG. 2 Volume of Solvent to Be Added to Complete Titration versus Volume of Diluent Used to Reach Initial End Point

concentration at both the initial and the second end points as follows:

$$\text{Dilution ratio} = A/B$$

$$\text{Cellulose nitrate concentration per 100 mL of volatile matter} = C/(A + B)$$

where:

A = diluent for the titration, mL,

B = solvent used, mL, and

C = cellulose nitrate used, g.

10.2 Construct a graph for dilution ratio versus cellulose nitrate concentration. Plot as two points on the graph (Fig. 3) the two sets of values calculated as described in 10.1. One of the points will be very close to 8 g/100 mL of volatile matter.

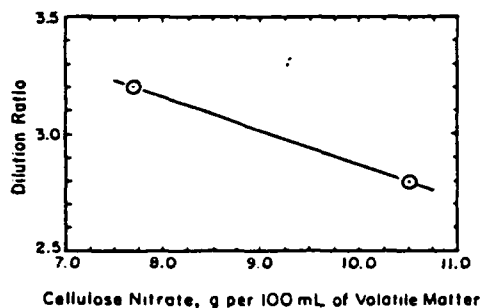


FIG. 3 Grams of Cellulose Nitrate per 100 mL of Volatile Matter versus Dilution Ratio

The correct value at exactly 8 g/100 mL of volatile matter may be interpolated by drawing a straight line connecting the two experimentally determined points. While the curve showing the relationship between the dilution ratio and cellulose nitrate concentration is not necessarily a straight line, the error made by interpolating or extrapolating from the straight line connecting the two points is negligible in the proximity of  $8 \pm 1$  g/100 mL of volatile matter.

NOTE 6: Example—Assuming a probable dilution ratio of approximately 3, the following results are obtained:

|  | Initial<br>End<br>Point | Solvent<br>Added<br>(from<br>Fig. 2) | Second<br>End<br>Point |
|--|-------------------------|--------------------------------------|------------------------|
| Cellulose nitrate, g                               | 5.00                    | ...                                  | 5.00                   |
| Solvent, mL  | 12.5                    | 3                                    | 15.5                   |
| Diluent, mL  | 35.0                    | ...                                  | 49.6                   |
| Solvent plus diluent, mL                           | 47.5                    | ...                                  | 65.1                   |
| Dilution ratio                                     | $35/12.5 = 2.8$         | ...                                  | $49.6/15.5 = 3.2$      |
| Cellulose nitrate per 100 mL of volatile matter, g | 10.5                    | ...                                  | 7.7                    |

From Fig. 3 the dilution ratio at 8.0 g of cellulose nitrate = 3.16

## 11. Report

11.1 When testing solvents, report the ratio of the volume of toluene to the volume of solvent at 8 g of cellulose nitrate per 100 mL of volatile matter.

11.2 When testing diluents, report the ratio of the volume of diluent to the volume of *n*-butyl acetate at 8 g of cellulose nitrate per 100 mL of volatile matter.

11.3 When testing cellulose nitrate, report the ratio of the volume of toluene to the volume of *n*-butyl acetate at 8 g of cellulose nitrate per 100 mL of volatile matter.

## 12. Precision and Bias

12.1 Precision—The following criteria should be used for judging the acceptability of results at the 95 % confidence level.

12.1.1 Repeatability—Two results obtained by the same operator should be considered suspect if they differ by more than 0.1.

12.1.2 Reproducibility—Two results obtained by operators in different laboratories should be considered suspect if they differ by more than 0.2.

12.2 Bias has not been determined for this test method.

The American Society for Testing and Materials takes no position respecting the validity of any patent rights asserted in connection with any item mentioned in this standard. Users of this standard are expressly advised that determination of the validity of any such patent rights, and the risk of infringement of such rights, are entirely their own responsibility.

This standard is subject to revision at any time by the responsible technical committee and must be reviewed every five years and if not revised, either reapproved or withdrawn. Your comments are invited either for revision of this standard or for additional standards and should be addressed to ASTM Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend. If you feel that your comments have not received a fair hearing you should make your views known to the ASTM Committee on Standards, 1916 Race St., Philadelphia, PA 19103.

ASTM D 1343-86

Standard Test Method for Viscosity of Cellulose  
Derivatives by Ball-Drop Method

## Standard Test Method for Viscosity of Cellulose Derivatives by Ball-Drop Method<sup>1</sup>

This standard is issued under the fixed designation D 1343; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

This method has been approved for use by agencies of the Department of Defense to replace Method 4272-1 of Federal Test Method Standard No. F41A and for listing in the DoD Index of Specifications and Standards.

### 1. Scope

1.1 This test method describes the apparatus and general procedure for making ball-drop viscosity measurements on solutions of various cellulose derivatives. Instructions for sample preparation, solution concentration, and other details are discussed in the ASTM methods for the respective cellulose derivatives.

1.2 This test method is applicable to solutions of various cellulose derivatives having viscosities greater than 10 P, by using balls of various diameters and densities. Viscosity results are expressed preferably in poises.

1.3 In commercial practice, viscosities are often expressed in seconds using  $\frac{3}{32}$ -in. (2.38-mm) stainless steel balls.<sup>2</sup> When the viscosity is outside the practical range for these balls (75 to 300 P), the measurement can be made using a calibrated pipet viscometer or a different ball and calculating the observed viscosity to the corresponding time for a  $\frac{3}{32}$ -in. ball, even though it is a small fraction of a second.

1.4 *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.*

### 2. Referenced Documents

#### 2.1 ASTM Standards:

- D 301 Methods of Testing Soluble Cellulose Nitrate<sup>3</sup>
- D 445 Test Method for Kinematic Viscosity of Transparent and Opaque Liquids (and the Calculation of Dynamic Viscosity)<sup>4</sup>
- D 817 Methods of Testing Cellulose Acetate Propionate and Cellulose Acetate Butyrate<sup>3</sup>
- D 871 Methods of Testing Cellulose Acetate<sup>3</sup>

### 3. Summary of Method

3.1 A solution of the cellulose derivative is made in a suitable solvent and allowed to equilibrate at a chosen

temperature. A stainless steel or aluminum ball is dropped into the solution, and the time required for it to cover a measured distance in its fall is recorded. The viscosity of the solution can then be calculated in poise or recorded in seconds.

### 4. Significance and Use

4.1 This test provides an easy method of determining the viscosity of cellulose derivatives in a given solvent. The answers are in units commonly used in industrial practice. Such information is needed for cellulose derivatives that are to be extruded, molded, sprayed, or brushed as is or in solution.

### 5. Apparatus

5.1 *Constant-Temperature Water Bath*, glass-walled.

5.2 *Bottles and Caps*:

5.2.1 Bottles, round or square, conforming to the dimensional requirements shown in Table 1, shall be used. Screw caps of metal or phenolic plastic in sizes to fit the bottles and having aluminum foil or cardboard and cellophane liners may be used to close the bottles. Alternatively, rubber stoppers covered with aluminum or tin foil, may also be used as closures. In this latter case, solvent loss during measurement of viscosity can be minimized by removing the stopper, leaving the foil in place, and making a small hole in the center of the foil through which the balls may be dropped.

5.2.2 Timing marks shall be provided around each bottle or on the front and back of the glass-walled constant-temperature water bath, to avoid parallax errors. The lower timing mark shall be approximately 1.25 in. (32 mm) above the base of the bottle, and the upper mark shall be  $2.00 \pm 0.02$  in. ( $50.8 \pm 0.5$  mm) above the lower mark. A practical means of marking consists of wrapping a 2-in. strip of transparent sheeting around the water bath at the proper location. The edges of the sheeting may be darkened with crayon. A light located back of the water bath aids in observing the ball during its fall.

5.3 *Balls*—Unless specifically directed otherwise, balls of varying size and density shall be used, depending on the viscosity of the solution. Table 2 gives the useful ranges, approximate apparatus constants, and dimensions of several such balls. The exact diameter, weight, and density shall be determined accurately for each lot of balls used.

5.4 *Graduate*—A 50 or 100-ml graduated cylinder, having a round top opening that can be tightly stoppered, shall be used for determining the density of the solution in grams per millilitre.

5.5 *Stop Watch*—A stop watch reading to 0.2 s.

FIG. 1

|  | B |
|--|---|
| Capacity   |   |
| Weight, g  |   |
| Height, in                                       |   |
| Inside dia                                       |   |
| Side to s  |   |
| Corner to  |   |
| * Approx from the O. follows: round with cap 48- |   |

### 6. Calibr

6.1 Calibrating equipment used:

where:  
g = accuracy  
r = ball

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee D-1 on Paint and Related Coatings and Materials and is the direct responsibility of Subcommittee D01.36 on Cellulosics.

Current edition approved July 25, 1986. Published September 1986. Originally published as D 1343 - 54. Last previous edition D 1343 - 69 (1955).

<sup>2</sup> When a  $\frac{3}{32}$ -in. stainless steel ball is used, the viscosities in seconds should be practically the same as those obtained using the apparatus described in Section 11 of Methods D 871 - 48, and in Section 10 of Specifications D 301 - 50, which last appeared in the 1952 Annual Book of ASTM Standards, Part 4.

<sup>3</sup> Annual Book of ASTM Standards, Vol 06.02.

<sup>4</sup> Annual Book of ASTM Standards, Vol 05.01.



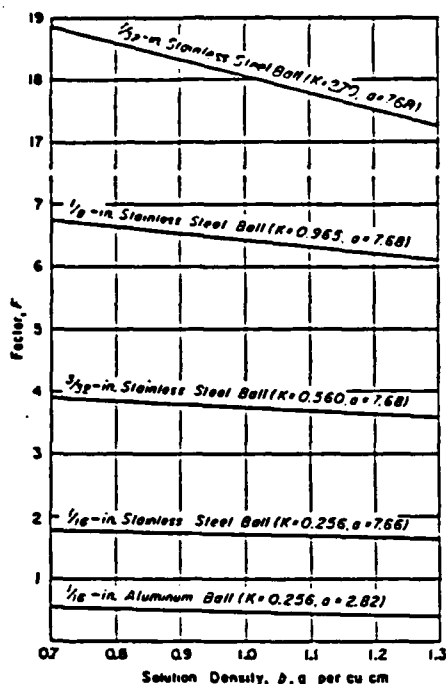


FIG. 1 Factors for Converting Viscosities in Seconds to Poises  
 $\eta = F \times t$

TABLE 1 Bottles<sup>a</sup>

| Bottle               | Round | Square |
|----------------------|-------|--------|
| Capacity, oz         | 16    | 16     |
| Weight, oz           | 12    | 12     |
| Height, in.          | 6.7   | 7      |
| Inside diameter, cm  | 6.4   |        |
| Side to side, cm     | ...   | 6.0    |
| Corner to corner, cm | ...   | 7.2    |

<sup>a</sup> Approximate sizes. Bottles satisfactory for this purpose may be obtained from the Owens Illinois Glass Co., Ohio Illinois Bldg., Toledo, Ohio, 43601, as follows: round bottle No. C-3145 with cap 63-400, French square bottle A-6732 with cap 48-400.

## 6. Calibration

6.1 Calculate the apparatus constant,  $K$ , using the following equation and exact dimensions of the bottle and balls used:

$$K = 2gr^2[1 - 2.104(d/D) + 2.09(d/D)^3]/9L$$

where:

$g$  = acceleration of gravity in cgs units

$r$  = ball radius, cm,

$d$  = ball diameter, cm.

$D$  = bottle diameter, cm (in the case of square bottles the average of the side to side and corner to corner diameters shall be used), and

$L$  = distance of ball drop, cm.

## 7. Procedure

7.1 *Preparation of Solution*—Dry the sample and prepare a solution as specified for the particular material. Such instructions are given in the viscosity sections of Methods D 301, D 871, and Methods D 817. Weigh into the bottle an appropriate amount of dry sample and specified solvent, accurate to 0.1 g, to make about 350 ml of solution. Close the bottle tightly. Allow to stand a short time for the solvent to penetrate the sample. Then tumble or shake until a uniform solution is obtained. Transfer to the water bath at  $25 \pm 0.1$  C, and allow the solution to come to temperature.

7.2 *Viscosity Determination*—Drop a  $3/32$ -in. (2.38-mm) stainless steel ball through the center of the column of solution and time its fall through the marked 2-in. (50.8-mm) distance, using a stop watch and taking precautions to avoid parallax errors. If the observed time is less than 20 s or greater than 100 s repeat the measurement, unless directed otherwise, using a different ball (see Table 2) which has a time of fall within these limits. If the solution is known to be thixotropic in nature or if the times of fall for successive balls vary significantly, use freshly prepared solutions for duplicate measurements or measurements with balls of other sizes.

7.3 *Determination of Lower Viscosities*—If the viscosity of the solution is too low to measure satisfactorily using one of the balls, use a calibrated pipet as described in Test Method D 445, or other instrument of suitable range. Calculate the result in poises. Convert poises to equivalent ball-drop seconds as shown in 8.2.

7.4 *Density Determination*—Determine the density of the solution in grams per cubic centimetre by measuring the volume at  $25 \pm 0.1$  C of a known weight of the solution contained in a suitable tightly stoppered graduated cylinder.

## 8. Calculation

8.1 *Ball-Drop Viscosities*—Calculate the viscosity in poises as follows:

$$\eta = K(a - b)t$$

where:

$\eta$  = viscosity at the specified temperature, P,

$K$  = apparatus constant,<sup>5</sup>

<sup>5</sup> See Table 2 for approximate values.

TABLE 2 Balls

| Ball                                 | Viscosity Range, P | Typical Data          |              |           |                                     |
|--------------------------------------|--------------------|-----------------------|--------------|-----------|-------------------------------------|
|                                      |                    | Apparatus Constant, K | Diameter, cm | Weight, g | Density, g/cm <sup>3</sup> , $\rho$ |
| 1/16-in. (1.59-mm) (aluminum)        | 10 to 50           | 0.256                 | 0.1588       | 0.00591   | 2.82                                |
| 1/16-in. (1.59-mm) (stainless steel) | 35 to 150          | 0.256                 | 0.1588       | 0.01605   | 7.66                                |
| 3/32-in. (2.38-mm)                   | 75 to 300          | 0.560                 | 0.2380       | 0.0542    | 7.68                                |
| 1/8-in. (3.18-mm)                    | 125 to 600         | 0.965                 | 0.3170       | 0.1277    | 7.68                                |
| 1/32-in. (5.56-mm)                   | 350 to 1800        | 2.70                  | 0.5556       | 0.6897    | 7.68                                |

$\rho$  = ball density<sup>5</sup>, in g/cm<sup>3</sup>,  
 $\rho_s$  = solution density, g/cm<sup>3</sup>, and  
 $t$  = time of fall, s.

In the case of a ball of stated diameter and density, this calculation can be simplified to:

$$\eta = F \times t,$$

where:  
 $F = K(a - b)$ .

This factor varies with solution density, b. Approximate factors for the various balls can be read from Fig. 1. Exact factors can be calculated from the exact measurements of the viscometer and balls.

8.2 *Poises to Seconds*—Poises may be converted to equivalent ball-drop seconds,  $t$ , as follows:

$$t(\text{for } \frac{3}{32}\text{-in. ball}) = \eta/K(a - b)$$

where:  
 $\eta$  = observed viscosity, P,  
 $K$  = apparatus constant for the  $\frac{3}{32}$  in. stainless steel ball,  
 $\rho$  = ball density for the  $\frac{3}{32}$ -in. stainless steel ball, and  
 $\rho_s$  = solution density for the solution being tested.

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*This standard is subject to revision at any time by the responsible technical committee and must be reviewed every five years and if not revised, either reapproved or withdrawn. Your comments are invited either for revision of this standard or for additional standards and should be addressed to ASTM Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend. If you feel that your comments have not received a fair hearing you should make your views known to the ASTM Committee on Standards, 1916 Race St., Philadelphia, PA 19103.*

## 9. Report

9.1 Results shall be reported in poises, or in seconds, for a  $\frac{3}{32}$ -in. stainless steel ball.

## 10. Precision and Bias

10.1 The within-laboratory precision of the test was determined by submitting 25 pairs of replicate samples to be run by any one of several operators. Each sample in a specific pair was submitted within 3 to 5 days. Each pair consisted of one sample at the 20-second viscosity level and one at the 60-second viscosity level. The data below shows the 95 % confidence limits (two sigma) for the two levels.

| Viscosity Level | 95 % Confidence Limits |
|-----------------|------------------------|
| 60 sec          | $\pm 3.83$ sec         |
| 20 sec          | $\pm 1.00$ sec         |

Data are not available at this time to show interlaboratory precision.

10.2 Since there is no accepted reference material suitable for determining the bias for the procedure in this test method for measuring ball-drop viscosity, no statement on bias can be made.



## 1. Scope

- 1.1 Test Method
- 1.2 Test Method

Moisture ...  
 Ash—as Sul ...  
 Chlorides ...  
 Alkalinity ...  
 Iron ...  
 Heavy Meta ...  
 Methoxyl Co ...  
 Viscosity:  
 Water-Sol ...  
 Alkali-Sol ...  
 pH ...  
 Solids ...  
 Density ...

## 2. Reference

- 2.1 ASTM D 96 Test Method for Water-Soluble Residues in Asphalts

## 3. Reagents

3.1 Purified water used in a test that all reagents used in the test are of the highest quality and are not lessening the accuracy of the test.

## 3.2 Unpurified water

## 4. Procedure

- 4.1 Test Method
- 0.01 g, to 0.001 g, in an oven at 105°C for 1 hour.

<sup>1</sup> These methods and Related Methods are included in the current edition of the *ASTM Annual Book of Standards*, Vol. 05.01, *Pharmaceuticals*, published by the American Society for Testing and Materials, 1916 Race St., Philadelphia, PA 19103.

ASTM D 1298-85

Standard Test Method for Density, Relative Density (Specific Gravity), or API Gravity of Crude Petroleum and Liquid Petroleum Products by Hydrometer Method



Designation: D 1298 - 85<sup>ε1</sup>

An American National Standard  
British Standard 4714



Designation: API MPMS Chapter 9.1



Designation: 160/82

# Standard Test Method for Density, Relative Density (Specific Gravity), or API Gravity of Crude Petroleum and Liquid Petroleum Products by Hydrometer Method<sup>1</sup>

This standard is issued under the fixed designation D 1298; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (<sup>ε</sup>) indicates an editorial change since the last revision or reapproval.

*This test method has been approved for use by agencies of the Department of Defense and for listing in the DoD Index of Specifications and Standards.*

*This test method was adopted as a joint ASTM-API-IP standard in 1968.*

<sup>ε1</sup> NOTE—An editorial change was made in Section 10.3 in November 1986.

## 1. Scope

1.1 This test method covers the laboratory determination, using a glass hydrometer, of the density, relative density (specific gravity), or API gravity of crude petroleum, petroleum products, or mixtures of petroleum and nonpetroleum products normally handled as liquids, and having a Reid vapor pressure (Test Method D 323, or IP 69) of (179 kPa) 26 lb or less. Values are measured on a hydrometer at convenient temperatures, readings of density being reduced to 15°C, and readings of relative density (specific gravity) and API gravity to 60°F, by means of international standard tables. By means of these same tables, values determined in any one of the three systems of measurement are convertible to equivalent values in either of the other two so that measurements may be made in the units of local convenience.

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.*

## 2. Referenced Documents

### 2.1 ASTM Standards:

D 323 Test Method for Vapor Pressure of Petroleum Products (Reid Method)<sup>2</sup>

D 1250 Petroleum Measurement Tables<sup>2</sup>

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee D-2 on Petroleum Products and Lubricants, the API Central Committee on Petroleum Measurement, and the IP Standardization Committee.

Current edition approved Oct. 25, 1985. Published December 1985. Originally published as D 1298 - 53 T. Last previous edition D 1298 - 80.

<sup>2</sup> Annual Book of ASTM Standards, Vol 05.01.

E 1 Specification for ASTM Thermometers<sup>3</sup>

E 100 Specification for ASTM Hydrometers<sup>3</sup>

## 3. Definitions

3.1 *density*—for the purpose of this test method, the mass (weight in vacuo) of liquid per unit volume at 15°C. When reporting results, explicitly state the density in units of mass (kilograms) and volume (litres), together with the standard reference temperature, for example, kilograms per litre at 15°C.

3.2 *relative density (specific gravity)*—for the purpose of this test method, the ratio of the mass of a given volume of liquid at 15°C (60°F) to mass of an equal volume of pure water at the same temperature. When reporting results, explicitly state the standard reference temperature, for example, relative density (specific gravity) 60/60°F.

3.3 *API gravity*—a special function of relative density (specific gravity) 60/60°F, represented by:

$$\text{API gravity, deg} = (141.5/\text{sp gr } 60/60^\circ\text{F}) - 131.5$$

No statement of reference temperature is required, since 60°F is included in the definition.

3.4 *observed values*—values observed at temperatures other than the specified reference temperature. These values are only hydrometer readings and not density, relative density (specific gravity), or API gravity at that other temperature.

## 4. Field of Application

4.1 The hydrometer method is most suitable for determining the density, relative density (specific gravity), or API gravity of mobile transparent liquids. It can also be used for viscous oils by allowing sufficient time for the hydrometer to

<sup>3</sup> Annual Book of ASTM Standards, Vols 05.03 and 14.03.

reach equilibrium, or for opaque oils by employing a suitable meniscus correction.

4.2 When used in connection with bulk oil measurements, volume correction errors are minimized by observing the hydrometer reading at a temperature close to that of the bulk oil temperature.

## 5. Summary of Method

5.1 The sample is brought to the prescribed temperature and transferred to a cylinder at approximately the same temperature. The appropriate hydrometer is lowered into the sample and allowed to settle. After temperature equilibrium has been reached, the hydrometer scale is read, and the temperature of the sample is noted. If necessary the cylinder and its contents may be placed in a constant temperature bath to avoid excessive temperature variation during the test.

## 6. Significance and Use

6.1 Accurate determination of the density, relative density (specific gravity), or API gravity of petroleum and its products is necessary for the conversion of measured volumes to volumes at the standard temperatures of 15°C or 60°F.

6.2 Density, relative density (specific gravity), or API gravity is a factor governing the quality of crude petroleum; crude petroleum prices are frequently posted against values in degrees API. However, this property of petroleum is an uncertain indication of its quality unless correlated with other properties.

## 7. Apparatus

7.1 *Hydrometers*, glass, graduated in units of density, relative density (specific gravity), or API gravity as required, conforming to ASTM specifications or specifications of the British Standards Institution as listed in Table 1.

7.2 *Thermometers*, having ranges shown in Table 2 and conforming to specifications of the American Society for Testing and Materials or the Institute of Petroleum.

7.3 *Hydrometer Cylinder*, clear glass, plastic (Note 1), or metal. For convenience in pouring, the cylinder may have a lip on the rim. The inside diameter of the cylinder shall be at least 25 mm greater than the outside diameter of the hydrometer used in it. The height of the cylinder shall be such that the appropriate hydrometer floats in the sample with at least 25-mm clearance between the bottom of the hydrometer and the bottom of the cylinder.

NOTE 1—Hydrometer cylinders constructed of plastic materials shall be resistant to discoloration or attack by oil samples and must not become opaque under prolonged exposure to sunlight and oil samples.

7.4 *Constant-Temperature Bath*, for use when the nature of the sample requires a test temperature much above or below room temperature or the requirements of 9.8 cannot otherwise be met.

NOTE 2—The user should ascertain that the instruments used for this test conform to the requirements set out above with respect to materials, dimensions, and scale errors. In cases where the instrument is provided with a calibration certificate issued by a recognized standardizing body, the instrument is classed as "certified" and the appropriate corrections listed shall be applied to the observed readings. Instruments which satisfy the requirements of this test method, but are not provided with a recognized calibration certificate, are classed as "uncertified."

## 8. Temperature of Test

8.1 The density, relative density (specific gravity), or API gravity by the hydrometer method is most accurate at or near the reference temperature of 15°C or 60°F. Use these or any other temperatures between -18 and +90°C (0 and 195°F), so far as it is consistent with the type of sample and necessary limiting conditions shown in Table 3.

8.2 When the hydrometer value is to be used to select multipliers for correcting volumes to standard temperatures, the hydrometer reading should be made preferably at a temperature within  $\pm 3^\circ\text{C}$  ( $\pm 5^\circ\text{F}$ ) of the temperature at which the bulk volume of the oil was measured (Note 3). However, in cases when appreciable amounts of light fractions may be lost during determination at the bulk oil temperature, the limits given in Table 3 should be applied.

NOTE 3—Volume and density (relative density (specific gravity), API gravity) correction tables are based on an average expansion for a number of typical materials. Since the same coefficients were used in computing both sets of tables, corrections made over the same temperature interval minimize error arising from possible differences between the coefficients of the material under test and the standard coefficients. This effect becomes more important as temperatures diverge significantly from 15°C (60°F).

## 9. Procedure

9.1 Adjust the temperature of the sample (Warning—Flammable. Vapor harmful. See Annex A1.1). Values are measured in accordance with the information given in Section 8. Bring the hydrometer cylinder (Note 4) and thermometer to approximately the same temperature as the sample to be tested.

NOTE 4—When testing completely opaque samples, metal hydrometer cylinders may be used. When such cylinders are used, accurate

TABLE 1 Recommended Hydrometers

| Specification                        | Type              | Units  | Range          |           | Scale    |              | Meniscus Correction |
|--------------------------------------|-------------------|--|----------------|-----------|----------|--------------|---------------------|
|                                      |                   |  | Total          | Each Unit | Interval | Error        |                     |
| BS 718:1960                          | special petroleum | density, kg/litre at 15°C                    | 0.600 to 1.100 | 0.050     | 0.0005   | $\pm 0.0003$ | + 0.0007            |
| L50 SP                               |                   |  | 0.600 to 1.100 | 0.050     | 0.001    | $\pm 0.0006$ | + 0.0014            |
| M50 SP                               | special petroleum | relative density (specific gravity) 60/60°F  | 0.600 to 1.100 | 0.050     | 0.0005   | $\pm 0.0003$ | + 0.0007            |
| BS 718:1960                          |                   |  | 0.600 to 1.100 | 0.050     | 0.001    | $\pm 0.0006$ | + 0.0014            |
| L50 SP                               |                   |  |                |           |          |              |                     |
| M50 SP                               | long, plain       | relative density (specific gravity), 60/60°F | 0.650 to 1.100 | 0.050     | 0.0005   | $\pm 0.0005$ |                     |
| Specification E 100, Nos. 82H to 90H |                   |  |                |           |          |              |                     |
| Specification E 100, Nos. 1H to 10H  | long, plain       | API  | -1 to + 101    | 12        | 0.1      | $\pm 0.1$    |                     |

TABLE 2 Recommended Thermometers

| Specification              | Type  | Scale | Range       | Graduation interval | Scale Error |
|----------------------------|---|-------|-------------|---------------------|-------------|
| IP 64 C                    | density, wide range                             | C     | -20 to +102 | 0.2                 | ± 0.1       |
| Specification E 1 No. 12 C | gravity   | C     | -20 to +102 | 0.2                 | ± 0.1       |
| IP 64 F                    | relative density (specific gravity), wide range | F     | -5 to +215  | 0.5                 | ± 0.25      |
| Specification E 1 No. 12 F | gravity   | F     | -5 to +215  | 0.5                 | ± 0.25      |

reading of the hydrometer can only be assured if the level of the sample is within 5 mm of the top of the cylinder.

9.2 Transfer the sample to a clean hydrometer cylinder without splashing, to avoid the formation of air bubbles, and to reduce to a minimum evaporation of the lower boiling constituents of more volatile samples. Transfer highly volatile samples to the cylinder by water displacement or by siphoning (Note 5). Remove any air bubbles formed, after they have collected on the surface of the sample, by touching them with a piece of clean filter paper before inserting the hydrometer.

NOTE 5—Highly volatile samples containing alcohols or other water-soluble material should always be transferred by siphoning.

9.3 Place the cylinder containing the sample in a vertical position in a location free from air currents. Ensure that the temperature of the sample does not change appreciably during the time necessary to complete the test; during this period, the temperature of the surrounding medium should not change more than 2°C (5°F). When testing at temperatures much above or below room temperature, a constant-temperature bath may be necessary to avoid excessive temperature changes.

9.4 Lower the hydrometer gently into the sample. Take care to avoid wetting the stem above the level to which it will be immersed in the liquid. Continuously stir the sample with the thermometer, taking care that the mercury thread is kept fully immersed and that the stem of the hydrometer is not wetted above the immersion level. As soon as a steady reading is obtained, record the temperature of the sample to the nearest 0.25°C (0.5°F) and then remove the thermometer.

9.5 Depress the hydrometer about two scale divisions into the liquid, and then release it. The remainder of the stem of the hydrometer, which is above the level of the liquid, must be kept dry since unnecessary liquid on the stem affects the reading obtained. With samples of low viscosity, impart a slight spin to the hydrometer on releasing to assist in bringing it to rest, floating freely away from the walls of the cylinder. Allow sufficient time for the hydrometer to come to rest, and for all air bubbles to come to the surface. This is particularly necessary in the case of more viscous samples.

9.6 When the hydrometer has come to rest, floating freely away from the walls of the cylinder (Note 6), estimate the hydrometer scale reading to the nearest 0.0001 relative density (specific gravity) or density or 0.05° API. The correct hydrometer reading is that point on the hydrometer scale at which the principal surface of the liquid cuts the scale. Determine this point by placing the eye slightly below the level of the liquid and slowly raising it until the surface, first seen as a distorted ellipse, appears to become a straight line cutting the hydrometer scale. (See Fig. 1.)

NOTE 6—When using a plastic cylinder, dissipate any static charge. Static charges often build up when using such cylinders and may prevent the hydrometer from floating freely.

9.7 With an opaque liquid take a reading by observing, with the eye slightly above the plane of the surface of the liquid, the point on the hydrometer scale to which the sample rises. This reading, at the top of the meniscus, requires correction since hydrometers are calibrated to be read at the principal surface of the liquid. The correction for the particular hydrometer in use may be determined by observing the maximum height above the principal surface of the liquid to which oil rises on the hydrometer scale when the hydrometer in question is immersed in a transparent oil having a surface tension similar to that of the sample under test (see Fig. 2).

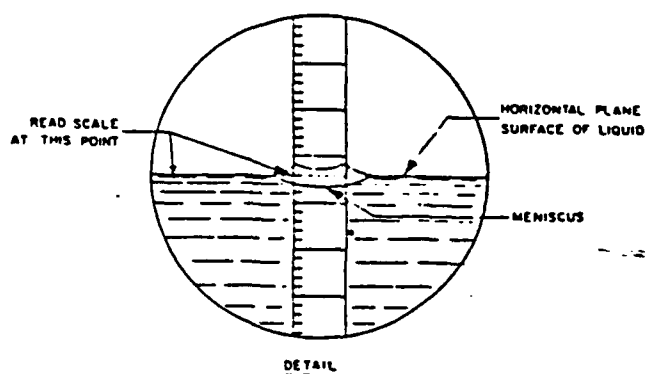
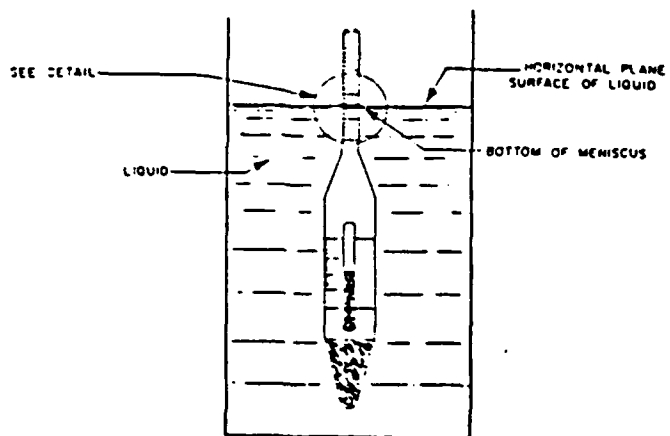
NOTE 7—Alternatively, corrections as given in Table 1 may be applied.

9.8 Immediately after observing the hydrometer scale value, again cautiously stir the sample with the thermometer keeping the mercury thread fully immersed. Record the temperature of the sample to the nearest 0.2°C (0.5°F) (Note 8). Should this temperature differ from the previous reading by more than 0.5°C (1°F), repeat the hydrometer test and then thermometer observations until the temperature becomes stable within 0.5°C (1°F).

NOTE 8—After use at a temperature higher than 38°C (100°F), allow all hydrometers of the lead shot in wax type to drain and cool in a vertical position.

TABLE 3 Limiting Conditions and Test Temperatures

| Sample Type                         | Initial Boiling Point   | Other Limits                      | Test Temperature   |
|-------------------------------------|-------------------------|-----------------------------------|--|
| Highly volatile                     |                         | Reid vapor pressure below 26 lb   | Cool in original closed container to 2°C (35°F) or lower             |
| Moderately volatile                 | 120°C (250°F) and below |                                   | Cool in original closed container to 18°C (65°F) or lower            |
| Moderately volatile and viscous     | 120°C (250°F) and below | viscosity too high at 18°C (65°F) | Heat to minimum temperature to obtain sufficient fluidity            |
| Nonvolatile                         | Above 120°C (250°F)     |                                   | Use any temperature between -18 and 90°C (0 and 175°F) as convenient |
| Mixtures with nonpetroleum products |                         |                                   | Test at 15 ± 0.2°C (60 ± 0.5°F)                                      |

FIG. 1 Hydrometer Scale Reading for Transparent Liquids<sup>4</sup>

## 10. Calculations and Report

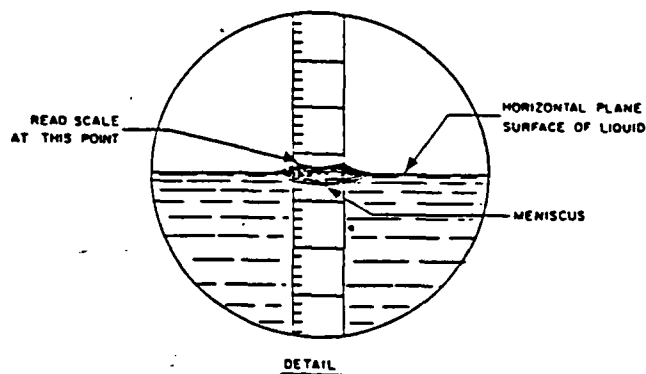
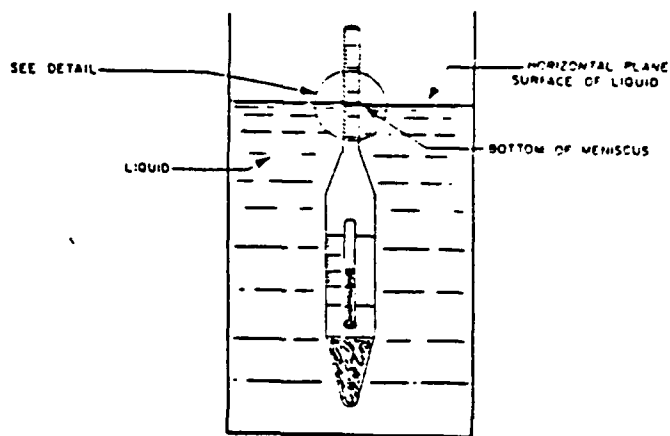
10.1 Apply any relevant corrections to the observed thermometer reading (for scale or bulb) and to the hydrometer reading (scale). For opaque samples, make the appropriate correction to the observed hydrometer reading as given in 9.7. Record to the nearest 0.0001 density or relative density (specific gravity) or 0.1° API the final corrected hydrometer scale reading (Note 9). After application of any relevant corrections record to the nearest 0.5°C or 1°F, the mean of the temperature values observed immediately before and after the final hydrometer reading.

NOTE 9—Hydrometer scale readings at temperatures other than calibration temperatures (15°C or 60°F) should not be considered as more than scale readings since the hydrometer bulb changes with temperature.

10.2 To convert corrected values from 10.1 to standard temperature, use the following from the Petroleum Measurement Tables (D 1250):

10.2.1 When a density scaled hydrometer has been employed, use Tables 53 A or 53 B to obtain density at 15°C.

10.2.2 When a relative density (specific gravity) hydrometer has been employed, use Tables 23 A or 23 B to obtain Relative Density (Specific Gravity) 60/60°F, and

FIG. 2 Hydrometer Scale Reading for Opaque Fluids<sup>4</sup>

10.2.3 When an API gravity scaled hydrometer has been employed, use Tables 5 A or 5 B to obtain the gravity in API degrees.

10.3 When a value is obtained with a hydrometer scaled in one of the units described herein and a result is required in one of the other units, make the conversion by one of the appropriate tables given in Standard D 1250, Petroleum Measurement Tables, Volume XI/XII. For conversion from density at 15°C, use Table 51; from relative density (specific gravity) 60/60°F, use Table 21; from API gravity, use Table 3.

10.4 Report the final value as density in kilograms per litre at 15°C, or as relative density (specific gravity) at 60/60°F, or as gravity in degrees API, as applicable.

## 11. Precision and Bias

11.1 The precision of the method as determined by statistical examination of interlaboratory results is as follows:

11.1.1 *Repeatability*—The difference between two test results, obtained by the same operator with the same apparatus under constant operating conditions on identical test material, would in the long run, in the normal and correct operation of the test method, exceed the following values only in one case in twenty:

<sup>4</sup> Editorial changes to Figs. 1 and 2 are presently underway.

# ASTM D 1298

| Product     | Temperature Range | Units                               | Repeatability | Product     | Temperature Range | Units                               | Reproducibility |
|-------------|-------------------|-------------------------------------|---------------|-------------|-------------------|-------------------------------------|-----------------|
| Transparent | -2 to 24.5°C      | density                             | 0.0005        | Transparent | -2 to 24.5°C      | density                             | 0.0012          |
| Nonviscous  | 29 to 76°F        | relative density (specific gravity) | 0.0005        | Nonviscous  | 29 to 76°F        | relative density (specific gravity) | 0.0012          |
|             | 42 to 78°F        | API gravity                         | 0.1           |             | 42 to 78°F        | API gravity                         | 0.3             |
| Opaque      | -2 to 24.5°C      | density                             | 0.0006        | Opaque      | -2 to 24.5°C      | density                             | 0.0015          |
|             | 29 to 76°F        | relative density (specific gravity) | 0.0006        |             | 29 to 76°F        | relative density (specific gravity) | 0.0015          |
|             | 42 to 78°F        | API gravity                         | 0.2           |             | 42 to 78°F        | API gravity                         | 0.5             |

11.1.2 *Reproducibility*—The difference between two single and independent results obtained by different operators working in different laboratories on identical test material would, in the long run, in the normal and correct operation of the test method, exceed the following values only in one case in twenty:

11.1.3 For very viscous products, or when the conditions given in 11.1.1 and 11.1.2 are not complied with, no specific variations can be given.

11.2 *Bias*—A statement of bias is being developed for this test method.

## ANNEX

### (Mandatory Information)

#### A1. PRECAUTIONARY STATEMENTS

##### A1.1 Petroleum Liquids

Warning—Flammable. Vapors harmful.

Keep away from heat, sparks, and open flame.

Keep container closed.

Use with adequate ventilation.

Avoid prolonged breathing of vapor.

Avoid prolonged or repeated skin contact.

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*This standard is subject to revision at any time by the responsible technical committee and must be reviewed every five years and if not revised, either reapproved or withdrawn. Your comments are invited either for revision of this standard or for additional standards and should be addressed to ASTM Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend. If you feel that your comments have not received a fair hearing you should make your views known to the ASTM Committee on Standards, 1916 Race St., Philadelphia, PA 19103.*



ASTM D 2196-86

Standard Test Methods for Rheological Properties of  
Non-Newtonian Materials by Rotational (Brookfield) Viscometer



# Standard Test Methods for Rheological Properties of Non-Newtonian Materials by Rotational (Brookfield) Viscometer<sup>1</sup>

This standard is issued under the fixed designation D 2196; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

These test methods have been approved for use by agencies of the Department of Defense to replace Method 4287 of Federal Test Method Standard No. 141A and for listing in the DoD Index of Specifications and Standards.

## 1. Scope

1.1 These test methods cover the determination of the apparent viscosity and the shear thinning and thixotropic properties of non-Newtonian materials in the shear rate range from 0.1 to 50  $s^{-1}$ .

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 the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

## 2. Referenced Document

### 2.1 ASTM Standard:

E 1 Specification for ASTM Thermometers<sup>2</sup>

## 3. Summary of Test Methods

3.1 Test Method A consists of determining the apparent viscosity of coatings and related materials by measuring the torque on a spindle rotating at a constant speed in the material.

3.2 Test Methods B and C consist of determining the shear thinning and thixotropic (time-dependent) rheological properties of the materials.<sup>3</sup> The viscosities of these materials are determined at a series of prescribed speeds of a rotational-type viscometer. The agitation of the material immediately preceding the viscosity measurements is carefully controlled.

## 4. Significance and Use

4.1 Test Method A is used for determining the apparent viscosity at a given rotational speed, although viscosities at two or more speeds better characterize a non-Newtonian material than does the single viscosity measurement.

4.2 With Test Methods B and C, the extent of shear thinning is indicated by the drop in viscosity with increasing viscometer speed. The degree of thixotropy is indicated by

comparison of viscosities at increasing and decreasing viscometer speeds (Test Method B), viscosity recovery (Test Method B), or viscosities before and after high shear (combination of Test Methods B and C). The high-shear treatment in Test Method C approximates shearing during paint application. The viscosity behavior measured after high shear is indicative of the characteristics of the paint soon after application.

## 5. Apparatus

5.1 Rotational-type viscometers having at least four speeds, such as:

5.1.1 Brookfield Viscometer,<sup>4</sup> Model LVF, having four rotational speeds, or Model LVT having eight rotational speeds, with set of four spindles; or

5.1.2 Brookfield Viscometer, Model RVF, having four rotational speeds, or Model RVT having eight rotational speeds, with set of seven spindles.

5.2 Thermometer—ASTM thermometer having a range from 20 to 70°C and conforming to the requirements for Thermometer 49C as prescribed in Specification E 1.

5.3 Containers, round 1-pt (0.5-L) can, 3 3/8 in. (85 mm) in diameter, or 1-qt (1-L) can, 4 in. (100 mm) in diameter.

5.4 Shaker,<sup>5</sup> or equivalent machine capable of vigorously shaking the test specimen.

## 6. Materials

6.1 Standard Oils,<sup>6</sup> calibrated in absolute viscosity, millipascal seconds.

## 7. Calibration of Apparatus

7.1 Select at least two standard oils of viscosities differing by at least 5 P (0.5 Pa·s) within the viscosity range of the material being measured and in the range of the viscometer. Condition the oils as closely as possible to 25.0°C (or other agreed-upon temperature) for 1 h in a 1-pt (0.5-L) can, 3 3/8 in. (85 mm) in diameter. Measure the viscosities of each oil as described in Test Method B (Section 13) taking readings only at increasing speeds (13.7). Make certain that the

<sup>1</sup> These test methods are under the jurisdiction of ASTM Committee D-1 on Paint and Related Coatings and Materials and are the direct responsibility of Subcommittee D01.24 on Physical Properties of Liquid Paints and Paint Materials.

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<sup>2</sup> Annual Book of ASTM Standards, Vol 14.01.

<sup>3</sup> Pierce, P. E., "Measurement of Rheology of Thixotropic Organic Coatings and Resins with the Brookfield Viscometer," *Journal of Paint Technology*, Vol 43, No. 557, 1971, pp. 35-43.

<sup>4</sup> Brookfield viscometers are available from the Brookfield Engineering Laboratories, Inc., 240 Cushing St., Stoughton, MA 02072.

<sup>5</sup> A reciprocating shaker may be obtained from the Red Devil Tools, 2400 Vauxhall Rd., Union, NJ 07083.

<sup>6</sup> Absolute viscosity standards are available in 1-pt samples from The Cannon Instrument Co., P.O. Box 16, State College, PA 16801, or Brookfield Engineering Laboratories, Inc., 240 Cushing St., Stoughton, MA 02072.

spindle is certified.

NOTE 1—T... with a spindle g... are designed for... conditions: RV... guard leg for sp... the same with...

7.1.1 Cali... with the LV... Calibration c... be done with... If the No. 1...

7.2 Comb... equal to the... temperature... able to assu...

Table 2 for... with temper... measurements are... should be c... measured. I...

stated value... calculate ne... follows:

where:

$f$  = new f... (mPa·s)

$V$  = viscos...

$S$  = scale...

7.3 Prep...

with the vis...

tions worke...

with speed.

TABLE 1

NOTE—M =

Speed, r

|     |
|-----|
| 0.5 |
| 1   |
| 2   |
| 2.5 |
| 4   |
| 5   |
| 10  |
| 20  |
| 50  |
| 100 |

n =

Speed, rpm

|     |
|-----|
| 0.3 |
| 0.6 |
| 1.5 |
| 3.0 |
| 6   |
| 12  |
| 30  |
| 60  |

spindle is centered in the container prior to taking measurements.

NOTE 1—The Brookfield LV and RV series viscometers are equipped with a spindle guard leg. The spindle/speed multiplying factors (Table 1) are designed for use with the guard leg in place except for the following conditions: RV series when the factors are the same with or without the guard leg for spindles No. 3 through 7; or LV series when the factors are the same with or without the guard leg for spindles No. 3 and 4.

7.1.1 Calibration in a 1-pt (0.5-L) can is always possible with the LV series viscometer with the guard leg attached. Calibration of the RV series viscometer in the 1-pt can must be done with spindles No. 3 through 7 without the guard leg. If the No. 1 or No. 2 spindles are to be used, calibration is carried out in the 1-qt (1-L) can with the guard leg attached.

7.2 Combining the tolerance of the viscometer ( $\pm 1\%$ , equal to the spindle/speed factor) and the tolerance of the temperature control (typically  $\pm 0.5^\circ\text{C}$  at  $25^\circ\text{C}$ ) it is reasonable to assume that a viscometer is calibrated if the calculated viscosities are within  $\pm 5\%$  of the stated values (see Table 2 for examples of the considerable change in viscosity with temperature exhibited by standard oils). If measurements are not made at  $25^\circ\text{C}$ , then the stated viscosities should be corrected to the temperature at which they are measured. If the viscosities determined in 7.1 differ from the stated values of the viscosity standard by more than  $5\%$ , calculate new factors for each spindle/speed combination as follows:

$$f = V/s \quad (1)$$

where:

$f$  = new factor for converting scale reading to viscosity, cP (mPa·s),

$V$  = viscosity of standard oil, mPa·s, and

$s$  = scale reading of the viscometer.

7.3 Prepare a table of new factors similar to that furnished with the viscometer (Table 1) for the spindle/speed combinations worked out in 7.2. Spindle/speed factors vary inversely with speed.

TABLE 1 Factors for Converting Brookfield Dial Readings to Centipoises (Millipascal Seconds)

NOTE—M = 1000.

| Speed, rpm | RV Series Factors Spindles |     |      |      |      |      |     |
|------------|----------------------------|-----|------|------|------|------|-----|
|            | 1                          | 2   | 3    | 4    | 5    | 6    | 7   |
| 0.5        | 200                        | 800 | 2000 | 4000 | 8000 | 20M  | 80M |
| 1          | 100                        | 400 | 1000 | 2000 | 4000 | 10M  | 40M |
| 2          | 50                         | 200 | 500  | 1000 | 2000 | 5M   | 20M |
| 2.5        | 40                         | 160 | 400  | 800  | 1600 | 4M   | 16M |
| 4          | 25                         | 100 | 250  | 500  | 1000 | 2.5M | 10M |
| 5          | 20                         | 80  | 200  | 400  | 800  | 2M   | 8M  |
| 10         | 10                         | 40  | 100  | 200  | 400  | 1M   | 4M  |
| 20         | 5                          | 20  | 50   | 100  | 200  | 500  | 2M  |
| 50         | 2                          | 8   | 20   | 40   | 80   | 200  | 800 |
| 100        | 1                          | 4   | 10   | 20   | 40   | 100  | 400 |

| Speed, rpm | LV Series Factors Spindles |      |      |     |
|------------|----------------------------|------|------|-----|
|            | 1                          | 2    | 3    | 4   |
| 0.3        | 200                        | 1000 | 4000 | 20M |
| 0.6        | 100                        | 500  | 2000 | 10M |
| 1.5        | 40                         | 200  | 800  | 4M  |
| 3.0        | 20                         | 100  | 400  | 2M  |
| 6          | 10                         | 50   | 200  | 1M  |
| 12         | 5                          | 25   | 100  | 500 |
| 30         | 2                          | 10   | 40   | 200 |
| 60         | 1                          | 5    | 20   | 100 |

## 8. Preparation of Specimen

8.1 Fill a 1-pt or 1-qt can with sample to within 1 in. (25 mm) of the top with the sample and bring it as close as possible to a temperature of  $25^\circ\text{C}$  or other agreed-upon temperature prior to test.

8.2 Vigorously shake the specimen on the shaker or equivalent for 10 min, remove it from the shaker, and allow it to stand undisturbed for 60 min at  $25^\circ\text{C}$  prior to testing (Note 2). Start the test no later than 65 min after removing the can from the shaker. Do not transfer the specimen from the container in which it was shaken.

NOTE 2—Shake time may be reduced if necessary, or as agreed upon between the purchaser and manufacturer, but, in any case, should not be less than 3 min.

## TEST METHOD A—APPARENT VISCOSITY

### 9. Procedure

9.1 Make all measurements as close as possible to  $25^\circ\text{C}$ , or other agreed-upon temperature.

9.2 Place the instrument on the adjustable stand. Lower the viscometer to a level that will immerse the spindle to the proper depth. Level the instrument using the attached spirit level.

9.3 Tilt the selected spindle (Note 3), insert it into one side of the center of the surface of the material, and attach the spindle to the instrument as follows: Firmly hold the upper shaft coupling with thumb and forefinger; screw left-hand thread spindle coupling securely to the upper shaft coupling being very careful when connecting to avoid undue side pressure which might affect alignment. Avoid rotating the dial so that pointer touches the stops at either extreme of the scale.

NOTE 3—Select the spindle/speed combination that will give a minimum scale reading of 10 but preferably in the middle or upper portion of the scale. The speed and spindle to be used may differ from this by agreement between user and producer.

9.4 Lower the viscometer until the groove (immersion mark) on the shaft just touches the material. Adjust the viscometer level if necessary. Move the container slowly in a horizontal plane until the spindle is located in approximately the center of the container so that the test will be run in a region undisturbed by the lowering of the spindle.

9.5 Turn on the viscometer. Adjust the viscometer to the rpm selected (Note 3) for the material under test. Allow the viscometer to run until the pointer has stabilized (Note 4). After the pointer has stabilized, depress the clutch and switch off the motor so that when it stops, the pointer will be in view (Note 5).

NOTE 4—In thixotropic paints, the pointer does not always stabilize. On occasion it reaches a peak and then gradually declines as the structure is broken down. In these cases, the time of rotation or number of revolutions prior to reading the viscometer should be agreed to

TABLE 2 Viscosity Variation of Cannon Viscosity Standards About the  $25^\circ\text{C}$  Temperature Point

| Cannon Viscosity Standard | Viscosity at $25^\circ\text{C}$ , cP (mPa·s) | Viscosity Change With $+1^\circ\text{C}$ at $25^\circ\text{C}$ , cP (mPa·s) |
|---------------------------|--|---|
| S-600                     | 1 400  | 87.7 (6.26 %)   |
| S-2000                    | 4 900  | 332 (6.77 %)  |
| S-8000                    | 20 000                                       | 1462.3 (7.31 %)   |

between user and manufacturer.

NOTE 5—Always release the clutch while the spindle is still immersed so that the pointer will float, rather than snap back to zero.

## 10. Calculation

10.1 Calculate the apparent viscosity at each speed, as follows:

$$V = fs$$

where:

$V$  = viscosity of sample in centipoises, mPa·s,

$f$  = scale factor furnished with instrument (see Table 1), and

$s$  = scale reading of viscometer.

## 11. Report

11.1 Report the following information:

11.1.1 The Brookfield viscometer model and spindle,

11.1.2 The viscosity at the spindle/speed utilized,

11.1.3 The specimen temperature in degrees celsius, and

11.1.4 The shake time and rest period, if other than specified.

## 12. Precision and Bias

12.1 *Precision*—See Section 23 for precision, including that for measurement at a single speed.

12.2 *Bias*—No statement of bias is possible with this test method.

## TEST METHOD B—VISCOSITY UNDER CHANGING SPEED CONDITIONS, DEGREE OF SHEAR THINNING AND THIXOTROPY

## 13. Procedure

13.1 Make all measurements with the Brookfield viscometer as close as possible to 25°C, or other agreed upon temperature.

13.2 Adjust the instrument and attach the spindle as in 9.2 through 9.4.

13.3 Set the viscometer at the slowest rotational speed (Notes 5 and 6). Start the viscometer and record the scale reading after ten revolutions (or other agreed-upon number of revolutions).

NOTE 6—When the eight speed viscometers (RVT and LVT) are used, lower or higher speeds than that permitted by the four speed viscometers may be used upon agreement between producer and user.

13.4 Increase the viscometer speed stepwise and record the scale reading after ten revolutions (or equivalent time for each spindle/speed combination) at each speed. After an observation has been made at the top speed, decrease the speed in steps to the slowest speed, recording the scale reading after ten revolutions (or equivalent time) at each speed.

NOTE 7—It is preferable to change speed when the motor is running.

13.5 After the last reading has been taken at the slowest speed, shut off the viscometer and allow it and the specimen to stand undisturbed for an agreed-upon rest period. At the end of the rest period, start the viscometer at the slowest speed and record the scale reading after ten revolutions (or other agreed-upon number of revolutions).

## 14. Calculations and Interpretation of Results

14.1 Calculate the apparent viscosity at each speed as shown in Section 9.

14.2 If desired, determine the degree of shear thinning by the following method:

14.2.1 *Shear Thinning Index* (sometimes erroneously called the thixotropic index)—Divide the apparent viscosity at a low rotational speed by the viscosity at a speed ten times higher. Typical speed combinations are 2 and 20 rpm, 5 and 50 rpm, 6 and 60 rpm but selection is subject to agreement between producer and user. The resultant viscosity ratio is an index of the degree of shear thinning over that range of rotational speed with higher ratios indicating greater shear thinning.

14.2.2 A regular or log-log plot of viscosity versus viscometer speed in rpm may also be useful in characterizing the shear-thinning behavior of the material. Such plots may be used for making comparisons between paints or other materials.

14.3 If desired, estimate the degree of thixotropy (under conditions of *limited* shearing-out of structure) by one of the following methods:

14.3.1 Calculate the ratio of the slowest speed viscosity taken with increasing speed to that with decreasing speed. The higher the ratio, the greater the thixotropy.

14.3.2 Calculate the ratio of the slowest speed viscosity taken after the rest period to that before the rest period. The higher the ratio, the greater the thixotropy.

## 15. Report

15.1 Report the following information:

15.1.1 The Brookfield viscometer and spindle,

15.1.2 The viscosities at increasing and decreasing spindle speeds,

15.1.3 The rest period time and the viscosity at the end of that time,

15.1.4 The specimen temperature in degrees celsius, and

15.1.5 The shake time if other than that specified.

15.2 *Optional Reporting*:

15.2.1 *Degree of Shear Thinning*—Shear thinning index and speeds over which it was measured (14.2).

15.2.2 *Estimated Degree of Thixotropy* (under conditions of shearing-out of structure)—Ratio of the lowest speed viscosities, for both increasing and decreasing speeds; or ratio of the lowest speed viscosities before and after the rest period, and speed at which they were measured (14.3).

## 16. Precision and Bias

16.1 *Precision*—See Section 23 for precision, including that for measurement of the shear thinning index (ratio of viscosity at 5 r/min to that at 50 r/min). It has not been possible to devise a method for determining precision for viscosities at increasing and decreasing speeds other than as individual measurements. No attempt was made to determine the precision of the measurement of the degree of thixotropy because this parameter is dependent on the material, the time of the test, and other variables.

16.2 *Bias*—No statement of bias is possible with this test method.

TEST MET

17. Apparatus  
17.1 High 2000 rpm circular disp

18. Preparation  
18.1 Inse: can (4.3) so bottom. Ru:

NOTE 8—A blades upon a

19. Procedure  
19.1 Imm: Method B in Section 9.

19.2 Star used in Test ten revolutions).  
19.3 Dec record the speed used after ten number of

20. Calcul:

20.1 As decreasing  
20.2 If the metho viscosity b paint imm solids).  
20.3 If conditions ating the shear. The Test Meth lowest spe higher the

7 Cowles o

# TEST METHOD C—VISCOSITY AND SHEAR THINNING OF A SHEARED MATERIAL

## 17. Apparatus

17.1 High-speed laboratory stirrer with speeds of at least 2000 rpm and equipped with a 2-in. (50-mm) diameter circular dispersion blade.<sup>7</sup>

## 18. Preparation of Specimen

18.1 Insert the 2-in. (50-mm) blade into the center of the can (4.3) so that the blade is about 1 in. (25 mm) from the bottom. Run the mixer at 2000 rpm (Note 8) for 1 min.

NOTE 8—Materials may be sheared at other speeds using other size blades upon agreement between producer and user.

## 19. Procedure

19.1 Immediately insert the same spindle used in Test Method B into the sheared material in the same manner as in Section 9.

19.2 Start the viscometer and adjust to the highest speed used in Test Method B (13.5). Record the scale reading after ten revolutions (or other agreed-upon number of revolutions).

19.3 Decrease the viscometer speed (Note 7) step-wise and record the scale readings at each speed down to the lowest speed used in Test Method B, recording the scale reading after ten revolutions at each speed (or other agreed-upon number of revolutions).

## 20. Calculations and Interpretation of Results

20.1 As in Test Method B, calculate the viscosities at each decreasing speed.

20.2 If desired, calculate the degree of shear thinning by the method given in Test Method B, 14.2. The measured viscosity behavior after shearing is essentially that of the paint immediately after application (disregarding changes in solids).

20.3 If desired, estimate the degree of thixotropy (under conditions of complete shearing-out of structure) by calculating the ratio of the lowest speed viscosities before and after shear. The lowest speed before-shear viscosity is taken from Test Method B, 14.1, at the lowest increasing speed. The lowest speed after-shear viscosity is taken from 20.1. The higher the ratio, the greater the thixotropy.

<sup>7</sup> Cowles or Shar type mixer/disperser.

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This standard is subject to revision at any time by the responsible technical committee and must be reviewed every five years and if not revised, either reapproved or withdrawn. Your comments are invited either for revision of this standard or for additional standards and should be addressed to ASTM Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend. If you feel that your comments have not received a fair hearing you should make your views known to the ASTM Committee on Standards, 1916 Race St., Philadelphia, PA 19103.

## 21. Report

21.1 Report the following information:

- 21.1.1 The Brookfield viscometer model and spindle,
- 21.1.2 The viscosities at decreasing spindle speeds,
- 21.1.3 The specimen temperature in degrees celsius, and
- 21.1.4 The speed of the high-speed mixer, size of blade, and time of mixing if different from method.

21.2 *Optional Reporting:*

21.2.1 *Degree of Shear Thinning*—Shear thinning index and speed over which it was measured (14.2).

21.2.2 *Estimated Thixotropy*—Ratio of lowest speed viscosities before and after shear and the speed at which they were measured.

## 22. Precision and Bias

22.1 *Precision*—The precision for individual viscosity measurements is the same as for Test Method A in Section 23. No attempt has been made to determine the precision of the shear thinning index or degree of thixotropy for Test Method C for the reasons given in 16.1.

22.2 *Bias*—No statement of bias is possible with this test method.

## 23. Summary of Precision

23.1 In an interlaboratory study of Test Methods A and B, eight operators in six laboratories measured on two days the viscosities of four architectural paints comprising a latex flat, a latex semi-gloss, a water-reducible gloss enamel, and an alkyd semi-gloss, that covered a reasonable range in viscosities and were shear thinning. Measurements at increasing speeds of 5, 10, 20, and 50 r/min (equivalent to eight operators testing 16 samples) were used to obtain the precision of Test Method A. The within-laboratory coefficient of variation for Test Method A (single speed) was found to be 2.49 % with 121 degrees of freedom and for Test Method B (Shear Thinning Index) 3.3 % with 31 degrees of freedom. The corresponding between-laboratories coefficients are 7.68 % with 105 degrees of freedom and 7.63 % with 27 degrees of freedom. Based on these coefficients the following criteria should be used for judging the acceptability of results at the 95 % confidence level:

23.1.1 *Repeatability*—Two results obtained by the same operator at different times should be considered suspect if they differ by more than 7 % relative for single speed viscosity and 9.5 % relative for shear thinning index.

23.1.2 *Reproducibility*—Two results obtained by operators in different laboratories should be considered suspect if they differ by more than 21.6 and 22.1 % relative, respectively, for the same two test methods.

ASTM D 93-85

Standard Test Methods for Flash Point  
by Pensky-Martens Closed Tester



Designation: D 93 - 85



Designation: 34/85

An American National Standard  
British Standard 2839  
American Association State  
Highway Transportation Standard  
AASHTO No. T73 - 811

## Standard Test Methods for Flash Point by Pensky-Martens Closed Tester<sup>1</sup>

This standard is issued under the fixed designation D 93; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

*These methods were adopted as a joint ASTM-IP Standard in 1967.*

*This method has been adopted for use by government agencies to replace Method 1102 of Federal Test Method Standard No. 791b, and Method 4293 of Federal Test Method Standard No. 141A.*

### 1. Scope

1.1 These test methods cover the determination of the flash point by Pensky-Martens closed-cup tester of fuel oils, lube oils, suspensions of solids, liquids that tend to form a surface film under test conditions, and other liquids.

NOTE 1—This method may be employed for the detection of contamination of lubricating oils by minor amounts of volatile materials.

NOTE 2—The U.S. Department of Transportation (DOT)<sup>2</sup> and U.S. Department of Labor (OSHA) have established that liquids with a flash point under 100°F (37.8°C) are flammable as determined by methods for those liquids which have a viscosity of 5.8 cSt or more at 100°F (37.8°C) or 9.5 cSt or more at 77°F (25°C), or that contain suspended solids, or have a tendency to form a surface film while under test. Other classification flash points have been established by these departments for liquids using this test.

1.2 Liquids having viscosities less than 5.5 cSt at 104°F (40°C) do not contain suspended solids or do not have a tendency to form a surface film while under test conditions should be tested in accordance with Method D 56.

1.3 *This standard should be used to measure and describe the properties of materials, products, or assemblies in response to heat and flame under controlled laboratory conditions and should not be used to describe or appraise the fire hazard or fire risk of materials, products, or assemblies under actual fire conditions. However, results of this test may be used as elements of a fire risk assessment which takes into account all of the factors which are pertinent to an assessment of the fire hazard of a particular end use.*

1.4 The values stated in inch-pound units shall be regarded as the standard.

1.5 *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.*

### 2. Referenced Documents

#### 2.1 ASTM Standards:

- D 56 Test Method for Flash Point by Tag Closed Tester<sup>3</sup>
- E 1 Specification for ASTM Thermometer<sup>4</sup>
- E 134 Specification for Pensky-Martens Closed Flash Tester<sup>5</sup>

### 3. Definition

3.1 *flash point*—the lowest temperature corrected to a barometric pressure of 101.3 kPa (760 mm Hg), at which application of a test flame causes the vapor of a specimen to ignite under specified conditions of test.

3.1.1 The sample is deemed to have flashed when a large flame appears and instantaneously propagates itself over the surface of the sample.

3.1.2 Occasionally, particularly near the actual flash point, the application of the test flame will cause a blue halo or an enlarged flame; this is not a flash and should be ignored.

### 4. Summary of Methods

4.1 The sample is heated at a slow, constant rate with continual stirring. A small flame is directed into the cup at regular intervals with simultaneous interruption of stirring. The flash point is the lowest temperature at which application of the test flame causes the vapor above the sample to ignite.

### 5. Significance and Use

5.1 Flash point measures tendency of the sample to form a flammable mixture with air under controlled laboratory conditions. It is only one of a number of properties which must be considered in assessing the overall flammability hazard of a material.

<sup>1</sup> These test methods are under the jurisdiction of ASTM Committee D-2 on Petroleum Products and Lubricants and are the direct responsibility of Subcommittee D02.08 on Volatility.

In the IP, these methods are under the jurisdiction of the Standardization Committee.

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<sup>2</sup> For information concerning regulations of U.S. Department of Transportation, see Codes of U.S. Regulations 49 CFR, Chapter I, and of U.S. Department of Labor, see 29 CFR, Chapter XVII. Each of these items is revised annually and may be procured from Superintendent of Documents, Government Printing Office, Washington, DC 20402.

<sup>3</sup> Annual Book of ASTM Standards, Vols 05.01 and 06.03.

<sup>4</sup> Annual Book of ASTM Standards, Vols 05.03 and 14.03.

<sup>5</sup> Annual Book of ASTM Standards, Vols 05.03 and 14.02.

5.2 Flash point is used in shipping and safety regulations to define "flammable" and "combustible" materials. One should consult the particular regulation involved for precise definitions of these classes.

5.3 Flash point can indicate the possible presence of highly volatile and flammable materials in a relatively nonvolatile or nonflammable material. For example, an abnormally low flash point on a sample of kerosine may indicate gasoline contamination.

## 6. Apparatus

6.1 *Pensky-Martens Closed Flash Tester*, as described in Annex A1.

NOTE 3—There are automatic flash point testers available and in use which may be advantageous in that they save testing time, permit the use of smaller samples, and exhibit other factors which may merit their use. If automatic testers are used, the user must be sure that all of the manufacturer's instructions for calibrating, adjusting, and operating the instrument are followed. In any cases of dispute the flash point as determined manually shall be considered the referee test.

6.2 *Thermometers*—Three standard thermometers shall be used with the ASTM Pensky-Martens tester as follows:

6.2.1 For tests in which the indicated reading falls within the limits of 50 to 140°F (10 to 60°C), inclusive, an ASTM 9F (9C) Pensky-Martens low range Thermometer having a range from 20 to 230°F (−5 to +110°C) and conforming to the requirements of Specification E 1 shall be used. Equally acceptable is IP thermometer 15F (15C), with specifications as shown in Annexes A2 and A3.

6.2.2 For tests in which the indicated reading falls within the limits 140 to 284°F (60 to 140°C), inclusive, an ASTM 88F (88C) Vegetable Oil Flash Thermometer having a range of 50 to 392°F (10 to 200°C) and conforming to the requirements of Specification E 1 shall be used.

6.2.3 For the range 140 to 230°F (60 to 110°C) either low or medium range thermometer may be used.

6.2.4 For tests in which the indicated reading falls within 265 to 700°F (130 to 370°C) an ASTM 10F (10C) Pensky-Martens high-range Thermometer having a range from 200 to 700°F (90 to 370°C) and conforming to the requirements of Specification E 1 shall be used. Equally acceptable is IP thermometer 16F (16C), with specifications as shown in Annex A3.

6.2.5 For the range 265 to 285°F (130 to 140°C) either the medium or high-range thermometer may be used.

## 7. Safety Precautions

7.1 The operator must exercise and take appropriate safety precautions during the initial application of the test flame, since samples containing low-flash material may give an abnormally strong flash when the test flame is first applied.

## 8. Sampling

8.1 Erroneously high flash points may be obtained if precautions are not taken to avoid the loss of volatile material. Do not open containers unnecessarily and make a transfer unless the sample temperature is at least the equivalent of 18°F (8°C) below the expected flash point. Do not use samples from leaky containers for these test methods.

8.2 Do not store samples in plastic (polyethylene, polypropylene, etc.) containers, since volatile material may diffuse through the walls of the enclosure.

## 9. Preparation of Apparatus

9.1 Support the tester on a level, steady table. Unless tests are made in a draft-free room or compartment, it is good practice, but not required, to surround the tester on three sides with a shield, each section of which is about 18 in. (450 mm) wide and 24 in. (600 mm) high. See Annex 14.3.1, 14.3.2, and 14.3.

NOTE 4—Caution—Meticulous attention to all details relating to the flame exposure device, size of test flame, rate of temperature increase, and rate of dipping the flame exposure device into the vapor of the specimen is necessary for good results.

## 10. Preparation of Sample

10.1 Samples of very viscous materials may be warmed until they are reasonably fluid before they are tested. However, no sample should be heated more than is absolutely necessary. It shall never be heated above a temperature of 30°F (17°C) below its expected flash point.

10.2 Samples containing dissolved or free water may be dehydrated with calcium chloride or by filtering through a qualitative filter paper or a loose plug of dry absorbent cotton. Warming the sample is permitted, but it shall not be heated for prolonged periods or above a temperature of 30°F (17°C) below its expected flash point.

NOTE 5—If the sample is suspected of containing volatile contaminants, the treatment described in 10.1 and 10.2 should be omitted.

## METHOD A—BASIC PROCEDURE

### 11. Procedure

11.1 Thoroughly clean and dry all parts of the cup and its accessories before starting the test, being sure to remove any solvent which had been used to clean the apparatus. Fill the cup with the sample to be tested to the level indicated by the filling mark. Place the lid on the cup and set the latter in the stove. Be sure to have the locating or locking device properly engaged. Insert the thermometer. Bring the material to be tested and the tester to a temperature of 60 ± 10°F (15 ± 5°C) or 20°F (11°C) lower than the estimated flash point, whichever is lower. Light the test flame and adjust it to 3/32 in. (4 mm) in diameter. Supply the heat at such a rate that the temperature as indicated by the thermometer increases 9 to 11°F (5 to 6°C)/min. Turn the stirrer 90 to 120 rpm, stirring in a downward direction.

11.2 If the sample is known to have a flash point of 230°F (110°C) or below, apply the test flame when the temperature of the sample is from 30°F (17°C) to 50°F (28°C) below the expected flash point and thereafter at a temperature reading that is a multiple of 2°F (1°C). Apply the test flame by operating the mechanism on the cover which controls the shutter and test flame burner so that the flame is lowered into the vapor space of the cup in 0.5 s, left in its lowered position for 1 s, and quickly raised to its high position. Do not stir the sample while applying the test flame.

11.3 If the sample is known to have a flash point above 230°F (110°C) apply the test flame in the manner just described at each temperature that is a multiple of 5°F (2°C),

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beginning at a temperature of 30°F (17°C) to 50°F (28°C) below the expected flash point.

NOTE 6—When testing materials to determine if volatile contaminants are present, it is not necessary to adhere to the temperature limits for initial flame application as stated in 11.2 and 11.3.

11.4 Record as the observed flash point the temperature read on the thermometer at the time the test flame application causes a distinct flash in the interior of the cup. Do not confuse the true flash point with the bluish halo that sometimes surrounds the test flame at applications preceding the one that causes the actual flash.

#### METHOD B—DETERMINATION OF FLASH POINT OF SUSPENSIONS OF SOLIDS AND HIGHLY VISCOUS MATERIALS

### 12. Procedure

12.1 Bring the material to be tested and the tester to a temperature of  $60 \pm 10^\circ\text{F}$  ( $15 \pm 5^\circ\text{C}$ ) or  $20^\circ\text{F}$  ( $11^\circ\text{C}$ ) lower than the estimated flash point, whichever is lower. Turn the stirrer  $250 \pm 10$  rpm, stirring in a downward direction. Raise the temperature throughout the duration of the test at a rate of not less than 2 nor more than  $3^\circ\text{F}$  ( $1$  to  $1.5^\circ\text{C}$ )/min. With the exception of these requirements for rates of stirring and heating, proceed as prescribed in Section 11.

### 13. Calculation and Report

13.1 Observe and record the ambient barometric pressure (Note 7) at the time of the test. When the pressure differs from 760 mm Hg (101.3 kPa), correct the flash point as follows:

- (A) Corrected flash point =  $C + 0.25 (101.3 - p)$   
 (B) Corrected flash point =  $F + 0.06 (760 - P)$   
 (C) Corrected flash point =  $C + 0.033 (760 - P)$

where:

- $F$  = observed flash points, °F,  
 $C$  = observed flash point, °C,  
 $P$  = ambient barometric pressure, mm Hg, and  
 $p$  = ambient barometric pressure, kPa.

NOTE 7—The barometric pressure used in this calculation must be the ambient pressure for the laboratory at the time of test. Many aneroid barometers, such as those used at weather stations and airports, are precorrected to give sea level readings. These must not be used.

13.2 Record the corrected flash point to the nearest 1°F (or 0.5°C).

13.3 Report the recorded flash point as the Pensky-Martens Closed Cup Flash Point ASTM D 93 - IP 34, of the sample tested.

### 14. Precision and Bias

14.1 *Method A*—The following criteria should be used for judging the acceptability of results (95 % probability):

14.1.1 *Repeatability*—Duplicate results by the same operator should be considered suspect if they differ by more than the following amounts:

| Material              | Flash Point Range, °F (°C) | Repeatability, °F (°C) |
|-----------------------|----------------------------|------------------------|
| Suspensions of solids | 95 to 110 (35 to 43)       | 4 (2)                  |
| All others            | 220 (104) and under        | 4 (2)                  |
|                       | Above 220 (104)            | 10 (5.5)               |

14.1.2 *Reproducibility*—The results submitted by each of two laboratories should be considered suspect if the two results differ by more than the following amounts:

| Material              | Flash Point Range, °F (°C) | Reproducibility, °F (°C) |
|-----------------------|----------------------------|--------------------------|
| Suspensions of solids | 95 to 110 (35 to 43)       | 6 (3.5)                  |
| All others            | 220 (104) and under        | 6 (3.5)                  |
|                       | Above 220 (104)            | 15 (8.5)                 |

14.2 *Method B*—The following criteria should be used for judging the acceptability of results (95 % confidence) obtained on viscous or heavily pigmented (paint or varnish) materials, or both, which tend to form a surface film:

14.2.1 *Repeatability*—The average of two tests by the same operator on the same day compared to the average of two tests on another day should be considered suspect if they differ by more than 9°F (5°C).

14.2.2 *Reproducibility*—The average of two tests by an operator on the same day compared to the average of two tests by another operator (or another laboratory) on any one day should be considered suspect if they differ by more than 18°F (10.0°C).

14.2.3 The definition of repeatability and reproducibility given here represents different parameters of the variance of the test methods; those given in 14.1 are derived from standards of ASTM Committee D-2 and the Institute of Petroleum, while those in 14.2 are from ASTM Committee D-1.

#### 14.3 Calibration of Tester:

14.3.1 Determine the flash point of the *p*-xylene,<sup>6</sup> following the directions in Sections 9 through 11. When the tester is operating properly, a value of  $81 \pm 2^\circ\text{F}$  ( $27.2 \pm 1.1^\circ\text{C}$ ) will be obtained.

14.3.2 If the flash point obtained on *p*-xylene is not within the limits stated in A4.1, check the condition and operation of the apparatus to ensure conformity with the details listed in Annex A1, especially with regard to the tightness of the lid (A1.1.2.1), the action of the shutter, and the position of the test flame (A1.1.2.2). After adjustment, if necessary, repeat the test. *P*-xylene having a flash point of  $81 \pm 2^\circ\text{F}$  ( $27.2 \pm 1.1^\circ\text{C}$ ) is not a suitable reference in the high-temperature range of the Pensky-Martens Closed Tester which may be as high as  $700^\circ\text{F}$  ( $370^\circ\text{C}$ ).

14.3.3 *p*-Xylene shall conform to the following requirements: Specific gravity  $15.56/15.56^\circ\text{C} \dots 0.860$  min,  $0.866$  max. Boiling range  $\dots 2^\circ\text{C}$  from start to dry, point when tested in accordance with Method D 850, or Method D 1078. The range shall include the boiling point of pure *p*-xylene which is  $138.35^\circ\text{C}$  ( $281.03^\circ\text{F}$ ). Purity  $\dots 95$  % min (freezing point of  $11.23^\circ\text{C}$ ), min calculated in accordance with Method D 1016, from the experimentally determined freezing point, measured by Method D 1015.

14.4 *Bias*—A bias statement is being developed for the test methods.

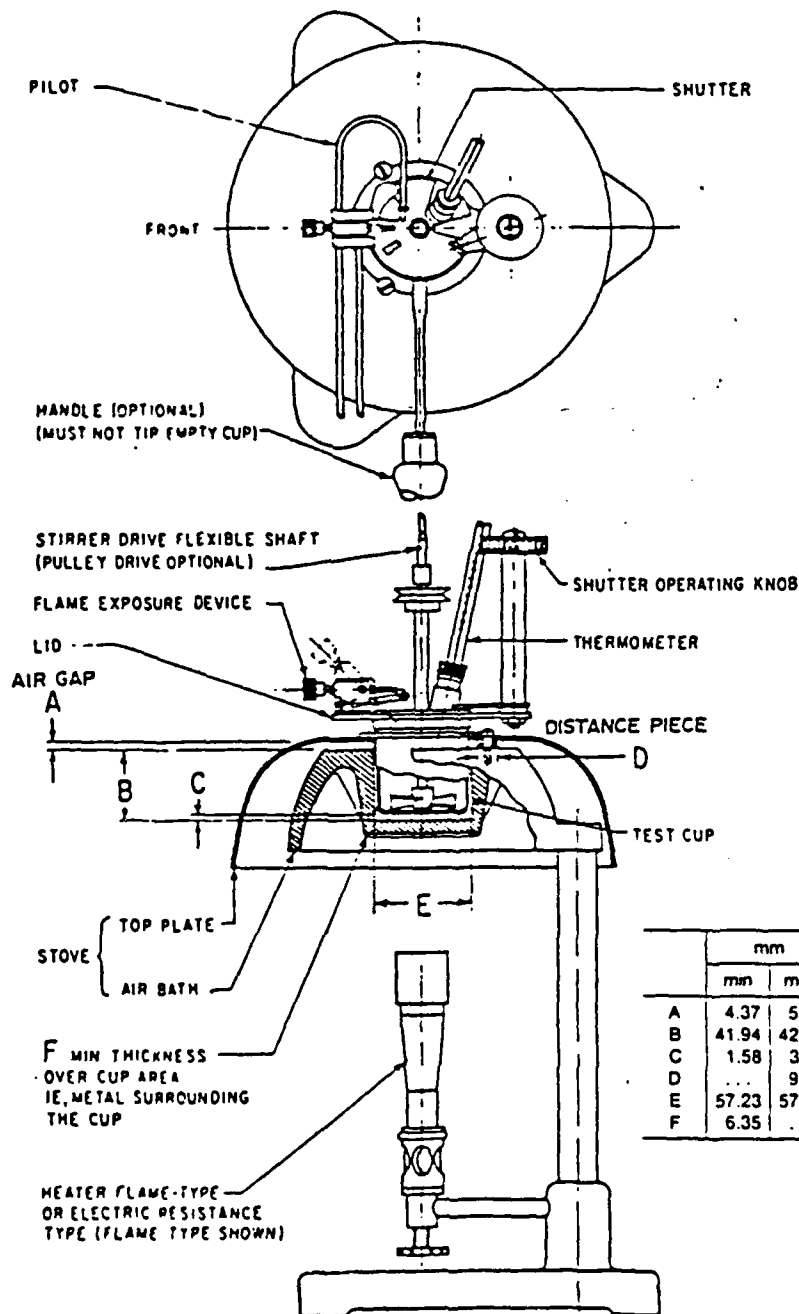
<sup>6</sup> Satisfactory *p*-xylene may be obtained as Flash Point Check Fluid from the Special Products Div., Chemical Dept., Phillips Petroleum Co., Drawer O, Burger, TX 79007.

# ANNEXES

(Mandatory Information)

## A1. APPARATUS SPECIFICATIONS

A1.1 A typical assembly of the apparatus, gas heated, is shown in Fig. A1.1. The apparatus shall consist of a test cup, cover, and stove conforming to the following requirements:



|   | mm    |       | in.   |       |
|---|-------|-------|-------|-------|
|   | min   | max   | min   | max   |
| A | 4.37  | 5.16  | 0.172 | 0.203 |
| B | 41.94 | 42.06 | 1.651 | 1.656 |
| C | 1.58  | 3.18  | 0.062 | 0.125 |
| D | ...   | 9.52  | ...   | 0.375 |
| E | 57.23 | 57.86 | 2.253 | 2.278 |
| F | 6.35  | ...   | 0.25  | ...   |

NOTE—Lid assembly may be positioned either right or left-handed.

FIG. A1.1 Pensky-Martens Closed Flash Tester

A1.1.1 *Cup*—The cup shall be of brass, or other nonrusting metal of equivalent heat conductivity, and shall conform to the dimensional requirements in Fig. A1.2. The flange shall be equipped with devices for locating the position of the cup in the stove. A handle attached to the flange of the cup is a desirable accessory. The handle shall not be so heavy as to tip over the empty cup.

A1.1.2 *Cover*:

A1.1.2.1 *Cover Proper*—The cover shown in Fig. A1.3 shall be of brass (A1.1.1) and shall have a rim projecting downward almost to the flange of the cup. The rim shall fit the outside of the cup with a clearance not exceeding 0.014 in. (0.36 mm) on the diameter. There shall be a locating or locking device, or both, engaging with a corresponding device on the cup. The four openings in the cover, A, B, C, and D, are shown in Fig. A1.3. The upper edge of the cup shall be in close contact with the inner face of the cover throughout its circumference.

A1.1.2.2 *Shutter*—The cover shall be equipped with a brass (Section 3) shutter (Fig. A1.4), approximately 3/32 in.

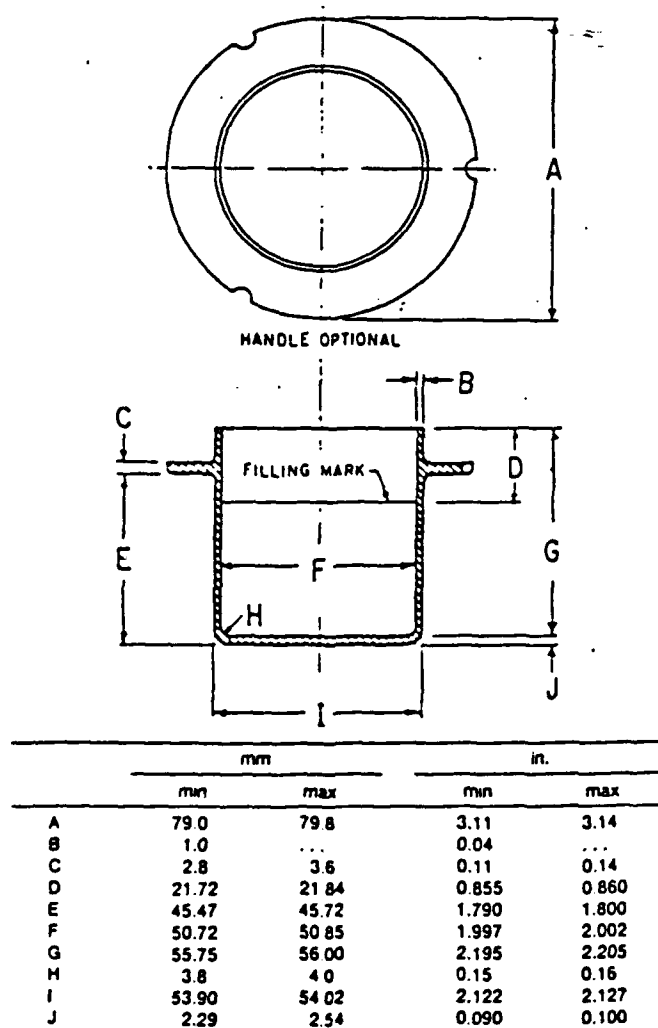


FIG. A1.2 Test Cup

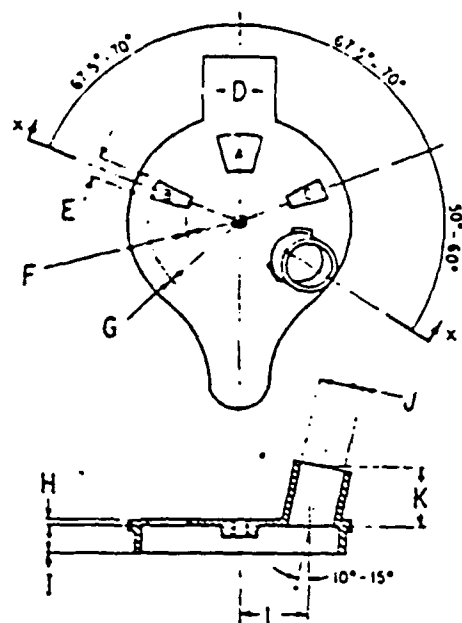
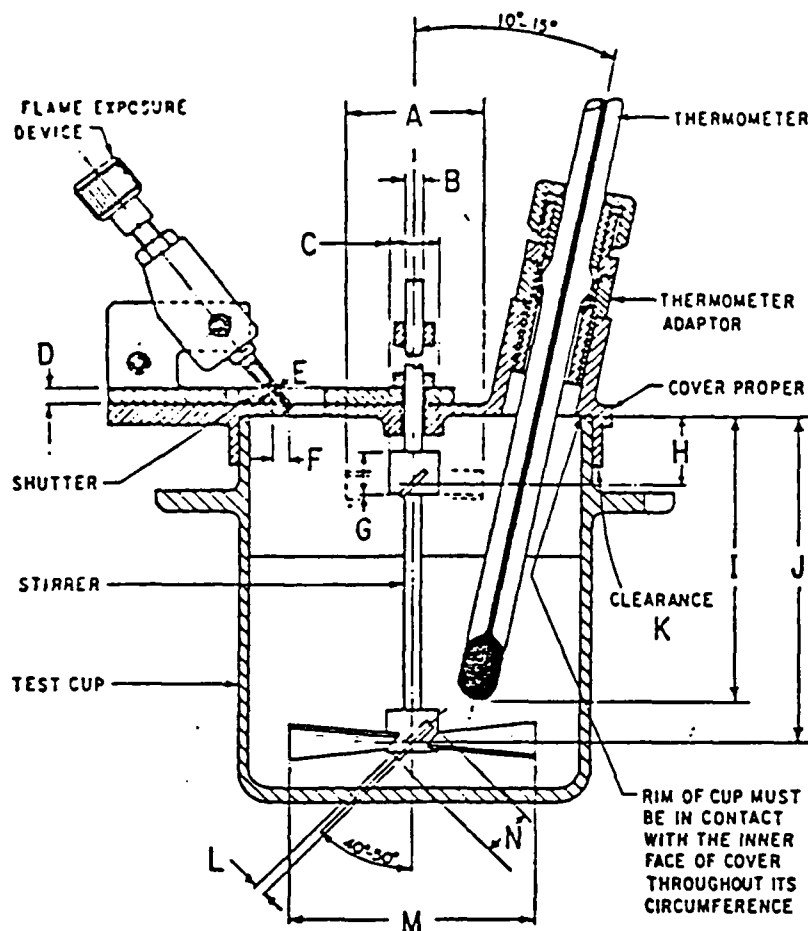


FIG. A1.3 Cover Proper

(2.4 mm) thick, operating on the plane of the upper surface of the cover. The shutter shall be so shaped and mounted that it rotates on the axis of the horizontal center of the cover between two stops, so placed, that when in one extreme position, the openings A, B, and C in the cover are completely closed, and when in the other extreme position, these openings are completely opened. The mechanism operating the shutter should be of the spring type and constructed so that when at rest the shutter shall exactly close the three openings. When operated to the other extreme, the three cover openings shall be exactly open and the tip of the exposure tube shall be fully depressed.

A1.1.2.3 *Flame-Exposure Device*—The flame-exposure device (Fig. A1.4) shall have a tip with an opening 0.027 to 0.031 in. (0.69 to 0.79 mm) in diameter. This tip shall be made preferably of stainless steel, although it may be fabricated of other suitable metals. The flame-exposure device shall be equipped with an operating mechanism which, when the shutter is in the "open" position, depresses the tip so that the center of the orifice is between the planes of the under and upper surfaces of the cover proper at a point on a radius passing through the center of the larger opening A (Fig. A1.3).

A1.1.2.4 *Pilot Flame*—A pilot flame shall be provided for automatic relighting of the exposure flame. A bead 3/32 in. (4



|                | mm   |      | in.   |       |
|----------------|------|------|-------|-------|
|                | min  | max  | min   | max   |
| A              | 18.3 | 19.8 | 0.72  | 0.78  |
| B              | 2.38 | 3.18 | 0.094 | 0.125 |
| C              | 7.6  | 8.4  | 0.30  | 0.33  |
| D              | 2.0  | 2.8  | 0.08  | 0.11  |
| E              | 0.69 | 0.79 | 0.027 | 0.031 |
| F              | 2.0  | 2.8  | 0.08  | 0.11  |
| G              | 6.4  | 10.4 | 0.25  | 0.41  |
| H              | 9.6  | 11.2 | 0.38  | 0.44  |
| I <sup>a</sup> | 43.0 | 46.0 | 1.69  | 1.81  |
| J              | 50.0 | 51.6 | 1.97  | 2.03  |
| K              | ...  | 0.36 | ...   | 0.014 |
| L              | 1.22 | 2.06 | 0.048 | 0.08  |
| M              | 31.8 | 44.4 | 1.25  | 1.75  |
| N              | 7.6  | 8.4  | 0.30  | 0.33  |

<sup>a</sup> Includes tolerance for length of thermometer given in Specification E 1.

FIG. A1.4 Test Cup and Cover Assembly

mm) in diameter may be mounted on the cover so that the size of the test flame can be regulated by comparison. The tip of the pilot flame shall have an opening the same size as the tip of the flame exposure device (0.027 to 0.031 in. (0.69 to 0.79 mm) in diameter).

**A1.1.2.5 Stirring Device**—The cover shall be equipped with a stirring device (Fig. A1.4) mounted in the center of the cover and carrying two 2-bladed metal propellers. In Fig. A1.4 lower propeller is designated by the letters L, M, and N. This propeller shall measure approximately 38 mm from tip

to tip, with each of its two blades 8 mm in width with a pitch of 45°. The upper propeller is designated by the letters A, C, and G. This propeller measures approximately 19 mm, tip to tip, each of its two blades is also 8 mm in width with a pitch of 45°. Both propellers are located on the stirrer shaft in such a manner that, when viewed from the bottom of the stirrer, the blades of one propeller are at 0 and 180° while the blades of the other propeller are at 90 and 270°. A stirrer shaft may be coupled to the motor by a flexible shaft or a suitable arrangement of pulleys.

A1.1.2.6 *Stove*—Heat shall be supplied to the cup by means of a properly designed stove which is equivalent to an air bath. The stove shall consist of an air bath and a top plate on which the flange of the cup rests.

A1.1.2.7 *Air Bath*—The air bath shall have a cylindrical interior and shall conform to the dimensional requirements in Fig. A1.1. The air bath may be either a flame or electrically heated metal casting (Note A1.1), or an electric-resistance element (Note A1.2). In either case, the air bath must be suitable for use at the temperatures to which it will be subjected without deformation.

NOTE A1.1—If the heating element is a flame or an electric heater, it shall be so designed and used that the temperatures of the bottom and the walls are approximately the same. In order that the air bath internal surfaces should be at a uniform temperature, it should not be less than  $\frac{1}{4}$  in. (6.4 mm) in thickness unless the heating element is designed to give

equal heat flux densities over all the wall and bottom surfaces.

NOTE A1.2—If the heater is of the electric resistance type, it shall be constructed so that all parts of the interior surface are heated uniformly. The wall and bottom of the air bath shall not be less than  $\frac{1}{4}$  in. (6.4 mm) in thickness unless the resistance heating elements are distributed over at least 80 % of the wall and all the bottom of the air bath. A heater having such a distribution of the heating elements positioned at least  $\frac{1}{2}$  in. (4.0 mm) away from the internal surface of the heating unit may be used in conjunction with a minimum thickness of  $\frac{1}{8}$  in. (1.58 mm) for the wall and bottom of the air bath.

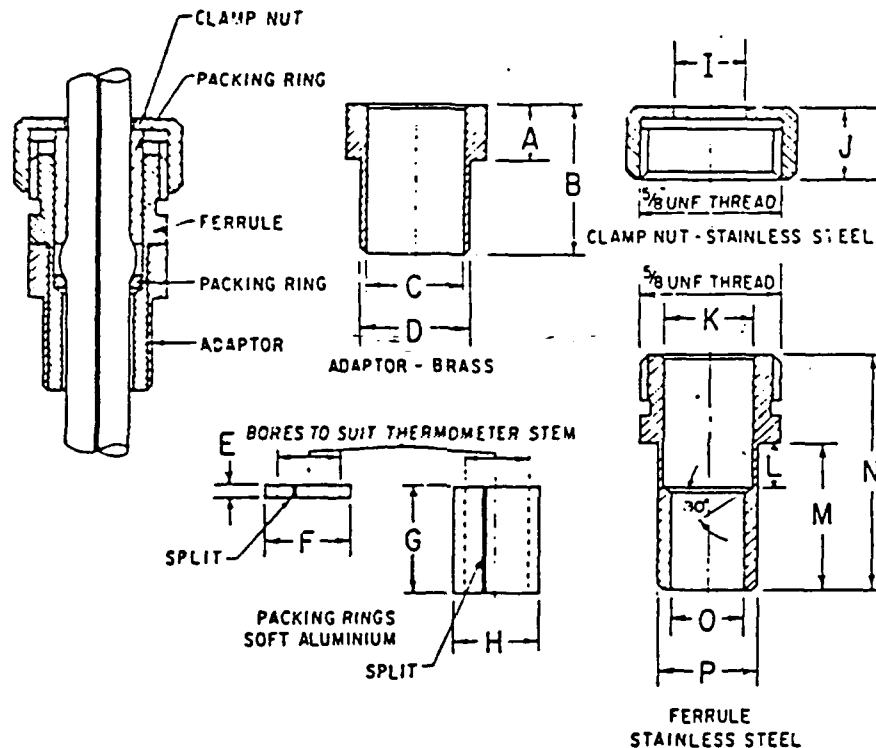
A1.1.2.8 *Top Plate*—The top plate shall be of metal, and shall be mounted with an air gap between it and the air bath. It may be attached to the air bath by means of three screws and spacing bushings. The bushings should be of proper thickness to define an air gap of  $\frac{3}{16}$  in. (4.8 mm), and they shall be not more than  $\frac{1}{4}$  in. (9.5 mm) in diameter.

## A2. MANUFACTURING STANDARDIZATION OF THERMOMETER AND FERRULE

A2.1 The low-range thermometer, which conforms also to the specification for the cup thermometer in the Tag closed tester (Test Method D 56) and which frequently is fitted with a metal ferrule intended to fit the collar on the cover of the Tag flash tester, can be supplemented by an adapter (Fig. A2.1) to be used in the larger diameter collar of the Pensky-Martens apparatus. Differences in dimensions of

these collars, which do not affect test results, are a source of unnecessary trouble to manufacturers and suppliers of instruments, as well as to users.

A2.2 Subcommittee 21 on Metalware Laboratory Apparatus, of ASTM Committee E-11 on Statistics, studied this problem and established some dimensional requirements which are shown in Fig. A2.1. Conformity to these requirements is not mandatory, but is desirable to users as well as suppliers of Pensky-Martens testers.



|   | mm    |       | in.   |       |
|---|-------|-------|-------|-------|
|   | min   | max   | min   | max   |
| A | 6.20  | 6.50  | 0.244 | 0.256 |
| B | 17.0  | 18.0  | 0.67  | 0.71  |
| C | 9.80  | 9.85  | 0.386 | 0.388 |
| D | 12.19 | 12.24 | 0.480 | 0.482 |
| E | 1.40  | 1.65  | 0.055 | 0.065 |
| F | 8.56  | 8.61  | 0.337 | 0.339 |
| G | 12.4  | 13.0  | 0.49  | 0.57  |
| H | 8.56  | 8.61  | 0.337 | 0.339 |
| I | 8.1   | 8.6   | 0.32  | 0.34  |
| J | 9.9   | 10.7  | 0.39  | 0.42  |
| K | 8.64  | 8.69  | 0.340 | 0.342 |
| L | 5.1   | 5.6   | 0.20  | 0.22  |
| M | 17.0  | 17.5  | 0.67  | 0.69  |
| N | 27.4  | 28.2  | 1.08  | 1.11  |
| O | 7.11  | 7.16  | 0.280 | 0.282 |
| P | 9.73  | 9.78  | 0.383 | 0.385 |

FIG. A2.1 Dimensions for Thermometer Adapter, Ferrule, and Packing Ring

### A3. THERMOMETER SPECIFICATIONS

TABLE A3.1 IP Thermometer Specifications

Note—The stem shall be made with an enlargement having a diameter of 1.5 to 2.0 mm greater than the stem and a length of 3 to 5 mm, the bottom of the enlargement being 64 to 66 mm from the bottom of the bulb. These dimensions shall be measured with the test gage shown in Fig. A3.1

| Name                               | IP 15F   | IP 15C   | IP 16F   | IP 16C   |
|------------------------------------|--|--|--|--|
|                                    | Pensky-Martens Low                                   |  | Pensky-Martens High                                  |  |
| Range                              | 20 to 230°F  | -7 to +110°C   | 200 to 700°F   | 90 to 370°C  |
| Graduation                         | 1°F  | 0.5°C  | 5°F  | 2°C  |
| Immersion, mm                      | 57   | 57   | 57   | 57   |
| Overall length ± 10 mm             | 280  | 280  | 280  | 280  |
| Stem diameter, mm                  | 5.5 to 7.0   | 5.5 to 7.0   | 5.5 to 7.0   | 5.5 to 7.0   |
| Bulb shape                         | cylindrical  | cylindrical  | cylindrical  | cylindrical  |
| Bulb length, mm                    | 9 to 13  | 9 to 13  | 10 max   | 10 max   |
| Bulb diameter, mm                  | not less than 5.5 and<br>not greater than<br>stem    | not less than 5.5 and<br>not greater than<br>stem    | not less than 5.5 and<br>not greater than<br>stem    | not less than 5.5 and<br>not greater than<br>stem    |
| Length of graduated portion,<br>mm | 143 to 177   | 143 to 177   | 143 to 177   | 143 to 177   |
| Distance bottom of bulb to,<br>mm  | 20°F<br>75 to 90                                     | -7°C<br>75 to 90                                     | 200°F<br>75 to 90                                    | 90°C<br>75 to 90                                     |
| Longer lines at each               | 5°F  | 1 and 5°C  | 25°F   | 10 and 20°C  |
| Figured at each                    | 10°F   | 5°C  | 50°F   | 20°C   |
| Expansion chamber                  | required   | required   | required   | required   |
| Top finish                         | ring   | ring   | ring   | ring   |
| Scale error not to exceed ±        | 1°F  | 0.5°C  | 2.5 to 500°F<br>3.5°F above 500°F                    | 1 to 260°C<br>2°C above 260°C                        |
| See notes                          | 1 and see table for<br>emergent stem<br>temperatures | 1 and see table for<br>emergent stem<br>temperatures | 1 and see table for<br>emergent stem<br>temperatures | 1 and see table for<br>emergent stem<br>temperatures |

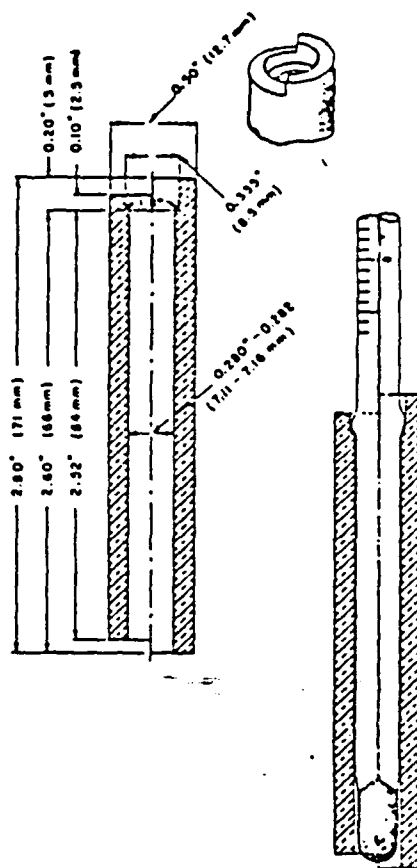


FIG. A3.1 Test Gage for Checking Enlargements on Thermometers



**TABLE A3.2 Specifications for ASTM Thermometers**  
All dimensions are in millimetres.  
See Table A3.3 for Standardization Temperature.



| ASTM No and Name  | Range           | For Test at | Im-<br>mer-<br>sion | Graduations            |                 |                     | Scale Error max | Special Inscrp-<br>tion               | Expan-<br>sion Cham-<br>ber |    | Total Length, ±5 | Stem OD          | Bulb                           |                          | Scale Location                 |                            |       |                                  | Ice Point Scale                   |                           | Contraction Chamber |        | Stem Enlargement             |                               |                |
|---|-----------------|-------------|---------------------|------------------------|-----------------|---------------------|-----------------|---------------------------------------|-----------------------------|----|------------------|------------------|--------------------------------|--------------------------|--------------------------------|----------------------------|-------|----------------------------------|-----------------------------------|---------------------------|---------------------|--------|------------------------------|-------------------------------|----------------|
|   |                 |             |                     | Sub-<br>divi-<br>sions | Long Lines Each | Num-<br>ber at Each |                 |                                       | Length                      | OD |                  |                  | Bot-<br>tom of Bulb to Line at | Dis-<br>tance to Line at | Bot-<br>tom of Bulb to Line at | Dis-<br>tance to Ice Point | Range | Bot-<br>tom of Bulb to Ice Point | Dis-<br>tance to Bot-<br>tom, min | Dis-<br>tance to Top, max | OD                  | Length | Dis-<br>tance to Bot-<br>tom |                               |                |
| 9C-62<br>Pensky<br>Marion<br>Low-Range<br>Tag Closed<br>Tester<br>9F-62 | -5 to<br>+110°C |             | 57                  | 0.5°C                  | 1°C             | 5°C                 | 0.5°C           | ASTM<br>9C or 9F<br>57 mm<br>IMM      | 160°C                       |    | 287              | 6.0<br>to<br>7.0 | 9.0<br>to<br>13                | 0°C<br>to<br>stem        | 85<br>to<br>98                 | 100°C<br>212°F             |       |                                  |                                   |                           |                     |        | 7.5<br>to<br>8.5             | 2.5<br>to<br>5.0 <sup>b</sup> | 64<br>to<br>66 |
| 10C-62<br>Pensky<br>Marion<br>High-Range<br>10F-62                      | 90 to<br>370°C  |             | 57                  | 2°C                    | 10°C            | 20°C                | 1°C             | ASTM<br>10C or<br>10F<br>57 mm<br>IMM | c                           |    | 287              | 6.0<br>to<br>7.0 | 8.0<br>to<br>10.0              | 4.5<br>to<br>6.0         | 86<br>to<br>99                 | 360°C<br>680°F             |       |                                  |                                   |                           |                     |        | 7.5<br>to<br>8.5             | 2.5<br>to<br>5.0 <sup>b</sup> | 64<br>to<br>66 |

<sup>a</sup> Scale error 1°C up to 260°C; 2°C over 260°C

<sup>b</sup> Scale error 2.5°F up to 500°F; 3.5°F over 500°F.

<sup>c</sup> An expansion chamber is provided for relief of gas pressure to avoid distortion of the bulb at higher temperatures. It is not for the purpose of joining mercury separations; and under no circumstances should the thermometer be heated above the highest temperature reading.

<sup>d</sup> The length of the enlargement, and the distance from the bottom of the enlargement to the bottom of the bulb shall be measured with the test gage shown in Fig A3.1.

TABLE A3.3 Standardization Temperatures

NOTE—The emergent column temperatures are those attained when using the thermometers in the test equipment for which the thermometers were originally designed. In some cases these temperatures are markedly different from those realized during standardization.

| Temperature                  | Average Temperature of Emergent Column | Temperature                   | Average Temperature of Emergent Column | Temperature                    | Average Temperature of Emergent Column | Temperature                   | Average Temperature of Emergent Column |
|------------------------------|--|-------------------------------|--|--------------------------------|--|-------------------------------|--|
| Thermometer 9F (20 to 230°F) |  | Thermometer 9C (-5 to +100°C) |  | Thermometer 10F (200 to 700°F) |  | Thermometer 10C (90 to 370°C) |  |
| 32°F                         | 66°F                                   | 0°C                           | 19°C                                   | 212°F                          | 141°F                                  | 100°C                         | 61°C                                   |
| 100°F                        | 86°F                                   | 35°C                          | 28°C                                   | 390°F                          | 159°F                                  | 200°C                         | 71°C                                   |
| 160°F                        | 106°F                                  | 70°C                          | 40°C                                   | 570°F                          | 180°F                                  | 300°C                         | 87°C                                   |
| 220°F                        | 123°F                                  | 105°C                         | 50°C                                   | 700°F                          | 220°F                                  | 370°C                         | 104°C                                  |
| IP 15F (20 to 230°F)         |  | IP 15C (-7 to 110°C)          |  | IP 16F (20 to 700°F)           |  | IP 16C (90 to 370°C)          |  |
| 32°F                         | 66°F                                   | 0°C                           | 19°C                                   | 200°F                          | 140°F                                  | 100°C                         | 61°C                                   |
| 70°F                         | 70°F                                   | 20°C                          | 20°C                                   | 300°F                          | 149°F                                  | 150°C                         | 65°C                                   |
| 100°F                        | 86°F                                   | 40°C                          | 31°C                                   | 400°F                          | 160°F                                  | 200°C                         | 71°C                                   |
| 150°F                        | 104°F                                  | 70°C                          | 40°C                                   | 500°F                          | 175°F                                  | 250°C                         | 78°C                                   |
| 212°F                        | 118°F                                  | 100°C                         | 48°C                                   | 600°F                          | 195°F                                  | 300°C                         | 87°C                                   |
|                              |  |                               |  | 700°F                          | 220°F                                  | 350°C                         | 99°C                                   |

TABLE A3.4 Specifications for Medium-Range Pensky-Martens

ASTM No. 88F (88C) Vegetable Oil Flash Thermometer

| Medium Range Pensky-Martens       |             |                               |          |
|-----------------------------------|-------------|-------------------------------|----------|
| 5                                 |             |                               |          |
| IP No.                            | 10-200°C    |                               | 50-392°F |
| Name                              |             |                               |          |
| Reference Fig. No.                |             |                               |          |
| Range                             |             |                               |          |
| For test at                       |             |                               |          |
| A Immersion, mm                   |             | 57                            |          |
| Graduations:                      |             |                               |          |
| Subdivisions                      | 0.5°C       |                               | 1°F      |
| Long lines at each                | 1°C and 5°C |                               | 5°F      |
| Numbers at each                   | 5°C         |                               | 10°F     |
| Scale error, max                  | 0.5°C       |                               | 1°F      |
| Special inscription               |             | ASTM<br>88F(88C)<br>57 mm IMM |          |
| Expansion chamber:                |             |                               |          |
| Permit heating to                 | 205°C       |                               | 400°F    |
| B Total length, mm                |             | 285 to 295                    |          |
| C Stem OD, mm                     |             | 6.0 to 7.0                    |          |
| D Bulb length, mm                 |             | 8.0 to 12.0                   |          |
| E Bulb OD, mm                     |             | >4.5 and <stem <sup>A</sup>   |          |
| Scale location:                   |             |                               |          |
| Bottom of bulb to line at         | 20°C        |                               | 68°F     |
| F Distance, mm                    |             | 80 to 90                      |          |
| G Length of graduated portion, mm |             | 145 to 180                    |          |
| Ice-point scale:                  |             |                               |          |
| Range                             |             |                               |          |
| H Bottom of bulb to ice-point, mm |             |                               |          |
| Contraction chamber:              |             |                               |          |
| I Distance to bottom, min, mm     |             |                               |          |
| J Distance to top, max, mm        |             |                               |          |
| Stem enlargement:                 |             |                               |          |
| K OD, mm                          |             | 7.5 to 8.5                    |          |
| L Length, mm                      |             | 2.5 to 5.0 <sup>A</sup>       |          |
| M Distance to bottom, mm          |             | 64 to 66                      |          |

<sup>A</sup> Bulb OD shall be greater than 4.5 mm and less than the outside diameter of the stem (C).

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This standard is subject to revision at any time by the responsible technical committee and must be reviewed every five years and if not revised, either reapproved or withdrawn. Your comments are invited either for revision of this standard or for additional standards and should be addressed to ASTM Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend. If you feel that your comments have not received a fair hearing you should make your views known to the ASTM Committee on Standards, 1916 Race St., Philadelphia, PA 19103.

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ASTM D 92-85

Standard Test Method for Flash and Fire Points  
by Cleveland Open Cup



Designation: D 92 - 85



Designation: 36/84

An American National Standard  
American Association of State  
Highway and Transportation Officials Standard  
AASHTO No. 748  
DIN 51 376

## Standard Test Method for Flash and Fire Points by Cleveland Open Cup<sup>1</sup>

This standard is issued under the fixed designation D 92; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

*This test method was adopted as a joint ASTM-IP standard in 1965.*

*This test method has been adopted for use by government agencies to replace Method 1103.7 of Federal Test Method Standard No. 791b, and Method 4294 of Federal Test Method Standard No. 141A.*

### 1. Scope

1.1 This test method covers determination of the flash and fire points of all petroleum products except fuel oils and those having an open cup flash below 175°F (79°C).

1.2 The values stated in inch-pound units are to be regarded as the standard.

NOTE 1—It is the practice in the United Kingdom and in many other countries to use IP Method 35, unless Test Method D 93 - IP 34 is specified. This test method may occasionally be specified for the determination of the fire point of a fuel oil. For the determination of the flash points of fuel oils, use Test Method D 93 - IP 34. Test Method D 93 - IP 34 should also be used when it is desired to determine the possible presence of small but significant concentrations of lower flash point substances which may escape detection by Test Method D 92. Test Method D 1310 may be employed if the flash point is below 175°F (79°C); as determined by Test Method D 92 - IP 36.

1.3 *This standard should be used to measure and describe the properties of materials, products, or assemblies in response to heat and flame under controlled laboratory conditions and should not be used to describe or appraise the fire hazard or fire risk of materials, products, or assemblies under actual fire conditions. However, results of this test may be used as elements of a fire risk assessment which takes into account all of the factors which are pertinent to an assessment of the fire hazard of a particular end use.*

1.4 *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.*

### 2. Referenced Documents

#### 2.1 ASTM Standards:

D 93 Test Method for Flash Point by Pensky-Martens Closed Tester<sup>2</sup>

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee D-2 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.08 on Volatility.

Current edition approved Oct. 25, 1985. Published December 1985. Originally published as D 92 - 21. Last previous edition D 92 - 78<sup>1</sup>.

In the IP, this test method is under the jurisdiction of the Standardization Committee.

<sup>2</sup> Annual Book of ASTM Standards, Vol 05.01.

D 1310 Test Method for Flash Point and Fire Point of Liquids by Tag Open-Cup Apparatus<sup>2</sup>

E 1 Specification for ASTM Thermometers<sup>3</sup>

#### 2.2 Other Method:

IP Method 35 Flash Point (Open) and Fire Point by Means of the Pensky-Martens Apparatus<sup>4</sup>

### 3. Definitions

3.1 *flash*—point the lowest temperature corrected to a barometric pressure of 101.3 kPa (760 mm Hg), at which application of a test flame causes the vapor of a specimen to ignite under specified conditions of test.

NOTE 2—The material is deemed to have flashed when a large flame appears and instantaneously propagates itself over the surface of the specimen.

Occasionally, particularly near the actual flash point, the application of the test flame will cause a blue halo or an enlarged flame; this is not a flash and should be ignored.

3.2 *fire point*—the lowest temperature at which a specimen will sustain burning for 5 s.

### 4. Summary of Method

4.1 The test cup is filled to a specified level with the sample. The temperature of the sample is increased rapidly at first and then at a slow constant rate as the flash point is approached. At specified intervals a small test flame is passed across the cup. The lowest temperature at which application of the test flame causes the vapors above the surface of the liquid to ignite is taken as the flash point. To determine the fire point, the test is continued until the application of the test flame causes the oil to ignite and burn for at least 5 s.

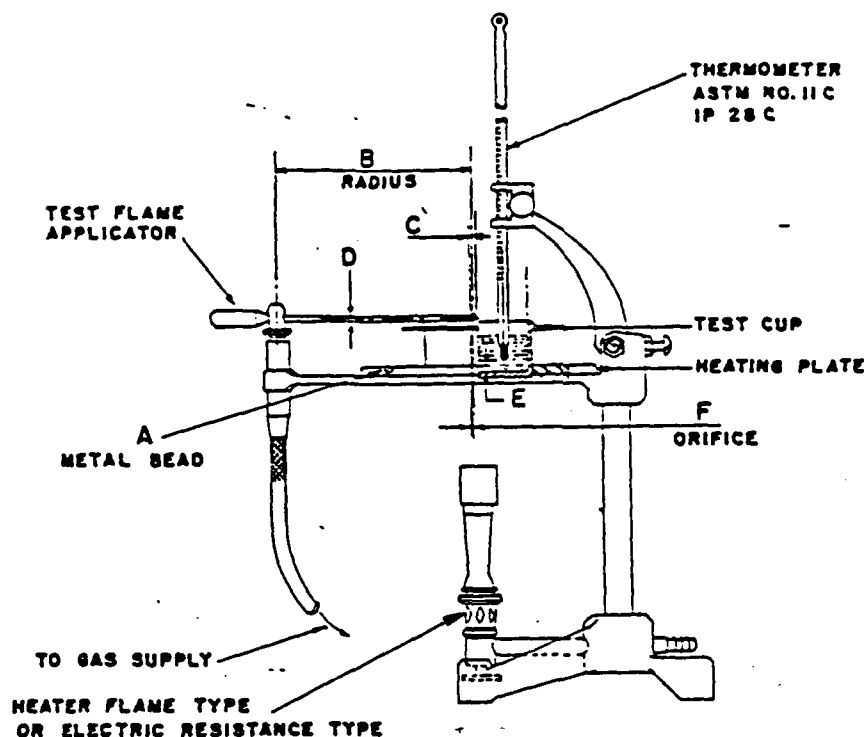
### 5. Significance and Use

5.1 Flash point measures the tendency of the sample to form a flammable mixture with air under controlled laboratory conditions. It is only one of a number of properties that must be considered in assessing the overall flammability hazard of a material.

5.2 Flash point is used in shipping and safety regulations to define "flammable" and "combustible" materials. One

<sup>3</sup> Annual Book of ASTM Standards, Vols 05.03 and 14.01.

<sup>4</sup> Available from the Institute of Petroleum, 61 New Cavendish St., London, W.1, England.



|            | min   | inches<br>max | min | millimetres<br>max |
|------------|-------|---------------|-----|--------------------|
| A—Diameter | 0.126 | 0.189         | 3.2 | 4.8                |
| B—Radius   | 6     | nominal       | 152 | nominal            |
| C—Diameter | 0.063 | 0.078         | 1.6 | nominal            |
| D          | 0.236 | 0.276         | 6   | 7                  |
| E—Diameter | 0.031 | nominal       | 0.8 | nominal            |

FIG. 1 Cleveland Open Cup Apparatus

should consult the particular regulation involved for precise definitions of these classes.

5.3 Flash point can indicate the possible presence of highly volatile and flammable materials in a relatively nonvolatile or nonflammable material.

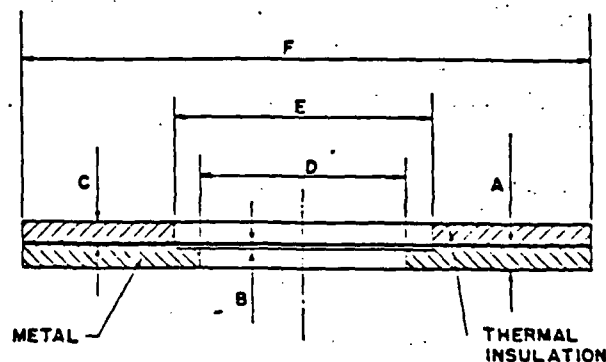
5.4 Fire point measures the characteristics of the sample to support combustion.

## 6. Apparatus

6.1 *Cleveland Open Cup Apparatus*—This apparatus consists of the test cup, heating plate, test flame applicator, heater, and supports described in detail in the annex. The assembled apparatus, heating plate, and cup are illustrated in Figs. 1, 2, and 3, respectively. Dimensions are listed in Tables 1, 2, and 3, respectively.

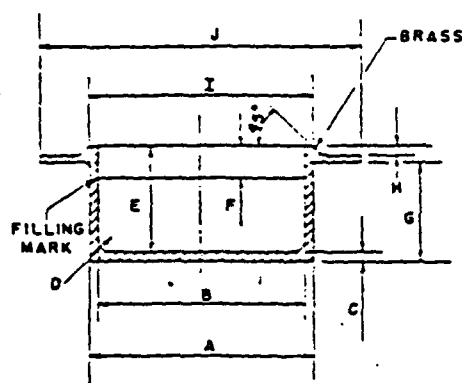
6.2 *Shield*—A shield 18 in. (460 mm) square and 24 in. (610 mm) high and having an open front is recommended.

6.3 *Thermometer*—A thermometer having a range as shown below and conforming to the requirements prescribed in Specification E 1 or in the Specifications for IP Standard Thermometers:



|            | min   | inches<br>max | min  | millimetres<br>max |
|------------|-------|---------------|------|--------------------|
| A          | 0.26  | 0.276         | 6    | 7                  |
| B          | 0.020 | 0.039         | 0.5  | 1.0                |
| C          | 0.236 | 2.276         | 6    | 7                  |
| D—Diameter | 2.165 | 2.205         | 55   | 56                 |
| E—Diameter | 2.736 | 2.776         | 69.5 | 70.5               |
| F—Diameter | 5.748 | 6.260         | 146  | 159                |

FIG. 2 Heating Plate



|          | inches |         | millimetres |         |
|----------|--------|---------|-------------|---------|
|          | min    | max     | min         | max     |
| A        | 2.658  | 2.717   | 67.5        | 69      |
| B        | 2.480  | 2.520   | 63          | 64      |
| C        | 0.110  | 0.138   | 2.8         | 3.5     |
| D—Radius | 0.157  | nominal | 4           | nominal |
| E        | 1.280  | 1.339   | 32.5        | 34      |
| F        | 0.354  | 0.394   | 9           | 10      |
| G        | 1.221  | 1.280   | 31          | 32.5    |
| H        | 0.110  | 0.138   | 2.8         | 3.5     |
| I        | 2.638  | 2.756   | 67          | 70      |
| J        | 3.819  | 3.937   | 97          | 100     |

FIG. 3 Cleveland Open Cup

| Temperature Range | Thermometer Number |     |
|-------------------|--------------------|-----|
|                   | ASTM               | IP  |
| 20 to 760°F       | 11F                | 28F |
| -6 to +400°C      | 11C                | 28C |

NOTE 3—There are automatic flash point testers available and in use which may be advantageous in the saving of testing time, permit the use of smaller samples, and have other factors which may merit their use. If automatic testers are used, the user must be sure that all of the manufacturer's instructions for calibrating, adjusting, and operating the instrument are followed. In any cases of dispute, the flash point as determined manually shall be considered the referee test.

## 7. Safety Precautions

7.1 The operator must exercise and take appropriate safety precautions during the initial application of the test flame, since samples containing low-flash material may give an abnormally strong flash when the test flame is first applied.

## 8. Sampling

8.1 Erroneously high flash points may be obtained if precautions are not taken to avoid the loss of volatile material. Do not open containers unnecessarily and make a transfer unless the sample temperature is at least the equivalent of 18°F (10°C) below the expected flash point. Do not use samples from leaky containers for this test.

8.2 Do not store samples in plastic (polyethylene, polypropylene, etc.) containers, since volatile material may diffuse through the walls of the enclosure.

8.3 Light hydrocarbons may be present in the form of gases, such as propane or butane and may not be detected by testing because of losses during sampling and loading of the test apparatus. This is especially evident on heavy residuums or asphalts from solvent extraction processes.

## 9. Preparation of Apparatus

9.1 Support the apparatus on a level steady table in a draft-free room or compartment. Shield the top of the apparatus from strong light by any suitable means to permit ready detection of the flash point. Tests made in a laboratory hood (Note 4) or in any location where drafts occur are not to be relied upon. During the last 30°F (17°C) rise in temperature prior to the flash point, care must be taken to avoid disturbing the vapors in the test cup by careless movements or breathing near the cup.

NOTE 4—With some samples whose vapors or products of pyrolysis are objectionable, it is permissible to place the apparatus with shield in a hood, the draft of which is adjustable so that vapors may be withdrawn without causing air currents over the test cup during the final 100°F (56°C) rise in temperature prior to the flash point.

9.2 Wash the test cup with an appropriate solvent to remove any oil or traces of gum or residue remaining from a previous test. If any deposits of carbon are present, they should be removed with steel wool. Flush the cup with cold water and dry for a few minutes over an open flame or a hot plate to remove the last traces of solvent and water. Cool the cup to at least 100°F (56°C) below the expected flash point before using.

9.3 Support the thermometer in a vertical position with the bottom of the bulb  $\frac{1}{4}$  in. (6.4 mm) from the bottom of the cup and locate at a point halfway between the center and side of the cup on a diameter perpendicular to the arc (or line) of the sweep of the test flame and on the side opposite to the test flame burner arm.

NOTE 5—The immersion line engraved on the thermometer will be  $\frac{3}{16}$  in. (2 mm) below the level of the rim of the cup when the thermometer is properly positioned.

## 10. Procedure

10.1 Fill the cup at any convenient temperature (Note 6) so that the top of the meniscus is exactly at the filling line. If too much sample has been added to the cup, remove the excess, using a medicine dropper; however, if there is sample on the outside of the apparatus, empty, clean, and refill it. Destroy any air bubbles on the surface of the sample.

NOTE 6—Viscous samples should be heated until they are reasonably fluid before being poured into the cup; however, the temperature during heating must not exceed 100°F (56°C) below the probable flash point.

10.2 Light the test flame and adjust it to a diameter of  $\frac{1}{8}$  to  $\frac{3}{16}$  in. (3.2 to 4.8 mm), the size of the comparison bead if one is mounted on the apparatus.

10.3 Apply heat initially so that the rate of temperature rise of the sample is 25 to 30°F (14 to 17°C)/min. When the sample temperature is approximately 100°F (56°C) below the anticipated flash point, decrease the heat so that the rate of temperature rise of the last 50°F (28°C) before the flash point is 9 to 11°F (5 to 6°C)/min.

10.4 Starting at least 50°F (28°C) below the flash point, apply the test flame when the temperature read on the thermometer reaches each successive 5°F (2°C) mark. Pass the test flame across the center of the cup, at right angles to the diameter which passes through the thermometer. With a smooth, continuous motion apply the flame either in a straight line or along the circumference of a circle having a radius of at least 6 in. (150 mm). The center of the test flame

must move (mm) above passing the flame across. The time in each case.

NOTE 7—Test flame size and rate of results.

10.5 Read on the scale on the side with the 100°F (56°C) rise in temperature prior to the flash point.

10.6 The sample temperature (°C) at least as observed.

## 11. Calculation

11.1 Correct time of the correct time following corrected or corrected where:

must move in a horizontal plane not more than  $\frac{1}{16}$  in. (2 mm) above the plane of the upper edge of the cup and passing in one direction only. At the time of the next test flame application, pass the flame in the opposite direction. The time consumed in passing the test flame across the cup in each case shall be about 1 s.

NOTE 7: Caution—Meticulous attention to all details relating to the test flame applicator, size of the test flame, rate of temperature increase, and rate of passing the test flame over the sample is necessary for good results.

10.5 Record as the observed flash point the temperature read on the thermometer when a flash appears at any point on the surface of the oil, but do not confuse the true flash with the bluish halo that sometimes surrounds the test flame.

10.6 To determine the fire point, continue heating so that the sample temperature increases at a rate of 9 to 11°F (5 to 6°C)/min. Continue the application of the test flame at 5°F (2°C) intervals until the oil ignites and continues to burn for at least 5 s. Record the temperature at this point as the observed fire point of the oil.

## 11. Calculation and Report

11.1 Observe and record the barometric pressure at the time of the test. When the pressure differs from 760 mm Hg, correct the flash or fire point, or both, by means of the following equations:

Corrected flash or fire point, or both =  $F + 0.06 (760 - P)$   
or Corrected flash or fire point, or both =  $C + 0.03 (760 - P)$   
where:

$F$  = observed flash or fire point, or both, to the nearest 5°F.  
 $C$  = observed flash or fire point, or both, to the nearest 2°C, and  
 $P$  = barometric pressure, mm Hg.

11.2 Record the corrected flash or fire point, or both, to the nearest 5°F or 2°C.

11.3 Report the recorded flash or fire point value, or both, as the COC flash or fire point, or both. ASTM D 92 - IP 36 of the sample tested.

## 12. Precision and Bias

12.1 The following data should be used judging the acceptability of results (95 % confidence).

12.1.1 Duplicate results by the same operator should be considered suspect if they differ by more than the following amounts:

| Repeatability |            |
|---------------|------------|
| Flash point   | 15°F (8°C) |
| Fire point    | 15°F (8°C) |

12.1.2 The result submitted by each of two laboratories should be considered suspect if the results differ by more than the following amounts:

| Reproducibility |             |
|-----------------|-------------|
| Flash point     | 30°F (17°C) |
| Fire point      | 25°F (14°C) |

12.2 Bias—The bias statement is being developed for this test method.

# ANNEX

(Mandatory Information)

## A1. APPARATUS FOR THE CLEVELAND OPEN TESTER

A1.1 *Test Cup*, conforming to Fig. 3 with dimensions as shown in Table 3. The cup shall be made of brass or other non-rusting metal of equivalent heat conductivity. The cup may be equipped with a handle.

A1.2 *Heating Plate*—A brass, cast iron, wrought iron, or steel plate with a center hole surrounded by an area of plane depression, and a sheet of hard asbestos board which covers the metal plate except over the area of plane depression in which the test cup is supported. The essential dimensions of the heating plate are shown in Fig. 2; however, it may be square instead of round, and the metal plate may have suitable extensions for mounting the test flame applicator device and the thermometer support. Also, a metal bead, as mentioned in A1.3, may be mounted on the plate so that it extends through and slightly above a suitable small hole in the asbestos board.

A1.3 *Test Flame Applicator*—The device for applying the flame may be of any suitable type, but it is suggested that the tip be approximately  $\frac{1}{16}$  in. (1.6 mm) in diameter at the end, and that the orifice be  $\frac{1}{4}$  in. (0.8 mm) in diameter. The device for operating the test flame may be mounted in such a manner as to permit automatic duplication of the sweep of the test flame, the radius of swing being not less than 6 in. (150 mm) and the center of the orifice being supported so

that it swings in a plane not greater than  $\frac{1}{4}$  in. (2 mm) above the plane of the rim of the cup. It is desired that a bead, having a diameter of  $\frac{1}{8}$  to  $\frac{3}{16}$  in. (3.2 to 4.8 mm) be mounted in a convenient position on the apparatus so that the size of the test flame can be compared to it.

A1.4 *Heater*—Heat may be supplied from any convenient source. The use of a gas burner or alcohol lamp is permitted, but under no circumstances are products of combustion or free flame to be allowed to come up around the cup. An electric heater controlled by a variable voltage transformer is preferred. The source of heat shall be centered under the opening of the heating plate with no local superheating. Flame-type heaters may be protected from drafts or excessive radiation by any suitable type of shield that does not project above the level of the upper surface of the asbestos board.

A1.5 *Thermometer Support*—Any convenient device may be used which will hold the thermometer in the specified position during a test and which will permit easy removal of the thermometer from the test cup upon completion of a test.

A1.6 *Heating Plate Support*—Any convenient support which will hold the heating plate level and steady may be employed.

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ASTM D 240-87

Standard Test Method for Heat of Combustion  
of Liquid Hydrocarbon Fuels by Bomb Calorimeter



## Standard Test Method for Heat of Combustion of Liquid Hydrocarbon Fuels by Bomb Calorimeter<sup>1</sup>

This standard is issued under the fixed designation D 240; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (<sup>e</sup>) indicates an editorial change since the last revision or reapproval.

*This test method has been adopted for use by government agencies to replace Method 2502 of Federal Test Method Standard No. 791b.*

<sup>1</sup> NOTE—An editorial correction was made in Section 10.2 in November 1988.

### 1. Scope

1.1 This test method<sup>2</sup> covers the determination of the heat of combustion of liquid hydrocarbon fuels ranging in volatility from that of light distillates to that of residual fuels.

1.2 Under normal conditions, this test method is directly applicable to such fuels as gasolines, kerosines, Nos. 1 and 2 fuel oil, Nos. 1-D and 2-D diesel fuel and Nos. 0-CT, 1-CT, and 2-CT gas turbine fuels.

1.3 The values stated in SI units are to be regarded as the standard.

1.4 *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 the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use. For specific hazard statements, see 7.5, 7.7, 7.8 and 9.3.*

### 2. Referenced Documents

#### 2.1 ASTM Standards:

D 129 Test Method for Sulfur in Petroleum Products (General Bomb Method)<sup>3</sup>

D 2382 Test Method for Heat of Combustion of Hydrocarbon Fuels by Bomb Calorimeter (High-Precision Method)<sup>4</sup>

E 1 Specification for ASTM Thermometers<sup>5</sup>

E 200 Practice for Preparation, Standardization, and Storage of Standard Solutions for Chemical Analyses<sup>6</sup>

### 3. Terminology

#### 3.1 Definitions:

3.1.1 *Gross Heat of Combustion*, expressed as megajoules per kilogram. The gross heat of combustion at constant volume of a liquid or solid fuel containing only the elements

carbon, hydrogen, oxygen, nitrogen, and sulfur is the quantity of heat liberated when a unit mass of the fuel is burned in oxygen in an enclosure of constant volume, the products of combustion being gaseous carbon dioxide, nitrogen, sulfur dioxide, and liquid water, with the initial temperature of the fuel and the oxygen and the final temperature of the products at 25°C.

3.1.2 *Net Heat of Combustion*, expressed as megajoules per kilogram. The net heat of combustion at constant pressure of a liquid or a solid fuel containing only the elements carbon, hydrogen, oxygen, nitrogen, and sulfur is the quantity of heat liberated when a unit mass of the fuel is burned in oxygen at a constant pressure of 0.101 MPa (1 atm), the products of combustion being carbon dioxide, nitrogen, sulfur dioxide, and water, all in the gaseous state, with the initial temperature of the fuel and the oxygen and the final temperature of the products of combustion at 25°C.

3.1.3 The following relationships may be used for converting to other units:

$$1 \text{ cal (International Table calorie)} = 4.1868 \text{ J}^4$$

$$1 \text{ Btu (British thermal unit)} = 1055.06 \text{ J}$$

$$1 \text{ cal (I.T.)}/\text{g} = 0.0041868 \text{ MJ}/\text{kg}^4$$

$$1 \text{ Btu}/\text{lb} = 0.002326 \text{ MJ}/\text{kg}^4$$

<sup>4</sup> Conversion factor is exact.

3.2 *Energy Equivalent* (effective heat capacity or water equivalent) of the calorimeter is the energy required to raise the temperature 1° expressed as MJ/°C.

3.2.1 *Description of Term Specific to This Standard*—The energy unit of measurement employed in this test method is the joule with the heat of combustion reported in megajoules per kilogram (Note 1).

$$1 \text{ MJ}/\text{kg} = 1000 \text{ J}/\text{g}$$

NOTE 1—In SI the unit of heat of combustion has the dimension J/kg, but for practical use a multiple is more convenient. The MJ/kg is customarily used for the representation of heats of combustion of petroleum fuels.

#### 3.3 Symbols:

3.3.1 The net heat of combustion is represented by the symbol  $Q_n$  and is related to the gross heat of combustion by the following equation:

$$Q_n (\text{net, } 25^\circ\text{C}) = Q_g (\text{gross, } 25^\circ\text{C}) - 0.2122 \times H$$

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee D-2 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.05 on Properties of Fuels, Petroleum, Coke and Oil Shale.

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<sup>2</sup> A more precise method designed specifically for use with aviation turbine fuels, although it can be used for a wide range of volatile and nonvolatile fuels is described in Test Method D 2382. *Annual Book of ASTM Standards*, Vol 05.02.

<sup>3</sup> *Annual Book of ASTM Standards*, Vol 05.01.

<sup>4</sup> *Annual Book of ASTM Standards*, Vol 05.02.

<sup>5</sup> *Annual Book of ASTM Standards*, Vols 05.03 and 14.03.

<sup>6</sup> *Annual Book of ASTM Standards*, Vol 15.05.

where:

$Q_n$  (net, 25°C) = net heat of combustion at constant pressure, MJ/kg

$Q_g$  (gross, 25°C) = gross heat of combustion at constant volume, MJ/kg

$H$  = mass % of hydrogen in the sample.

3.3.2 Temperatures may be measured in Celsius degrees.

NOTE 2—Temperatures may be recorded in either Fahrenheit degrees or ohms or other units when using electric thermometers. The same units must then be used in all calculations, including standardization.

3.3.3 Time is expressed in calculations in minutes and decimal fractions thereof. It may be measured in minutes and seconds.

3.3.4 Weights are measured in grams.

#### 4. Summary of Test Method

4.1 Heat of combustion is determined in this test method by burning a weighed sample in an oxygen bomb calorimeter under controlled conditions. The heat of combustion is computed from temperature observations before, during, and after combustion, with proper allowance for thermochemical and heat transfer corrections. Either isothermal or adiabatic calorimeter jackets may be used.

#### 5. Significance and Use

5.1 The heat of combustion is a measure of the energy available from a fuel. A knowledge of this value is essential when considering the thermal efficiency of equipment for producing either power or heat.

5.2 The heat of combustion as determined by this test method is designated as one of the chemical and physical requirements of both commercial and military turbine fuels and aviation gasoline.

5.3 The mass heat of combustion, the heat of combustion per unit mass of fuel, is a critical property of fuels intended for use in weight-limited craft such as airplanes, surface effect vehicles, and hydrofoils. The range of such craft between refueling is a direct function of the heat of combustion and density of the fuel.

#### 6. Apparatus

6.1 Test Room, Bomb, Calorimeter, Jacket, Thermometers, and Accessories, as described in Annex A1.

#### 7. Reagents

7.1 *Benzoic Acid, Standard*<sup>7</sup>—Benzoic acid powder must be compressed into a tablet or pellet before weighing. Benzoic acid pellets for which the heat of combustion has been determined by comparison with the National Bureau of Standards sample are obtainable commercially for those laboratories not equipped to pellet benzoic acid.

7.2 *Gelatin Capsules*.

7.3 *Methyl Orange or Methyl Red Indicator*.

7.4 *Mineral Oil*.

<sup>7</sup> Obtainable from the National Bureau Standards, Washington, DC 20234, as standard sample No. 39i.

7.5 *Oxygen*—Commercial oxygen produced from liquid air can be used without purification. If purification is necessary see Annex A1.11.

NOTE 3: Warning—Oxygen vigorously accelerates combustion. See Annex A3.2.

7.6 *Pressure-Sensitive Tape*<sup>8</sup>—Cellophane tape 38 mm (1½ in.) wide, free of chlorine and sulfur.

7.7 *Alkali, Standard Solution*:

7.7.1 *Sodium Hydroxide Solution* (0.0866 N)—Dissolve 3.5 g of sodium hydroxide (NaOH) in water and dilute to 1 L. Standardize with potassium acid phthalate and adjust to 0.0866 N as described in Method E 200.

NOTE 4: Warning—Corrosive. Can cause severe burns or blindness. Evolution of heat produces a violent reaction or eruption upon too rapid mixture with water. See Annex A3.1.

7.7.2 *Sodium Carbonate Solution* (0.0725 N)—Dissolve 3.84 g of Na<sub>2</sub>CO<sub>3</sub> in water and dilute to 1 L. Standardize with potassium acid phthalate and adjust to 0.0725 N as described in Method E 200.

7.8 *2,2,4-Trimethylpentane (isooctane), Standard*<sup>9</sup>

NOTE 5: Warning—Extremely flammable. Harmful if inhaled. Vapors may cause flash fire. See Annex A3.3.

#### 8. Standardization

8.1 Determine the energy equivalent of the calorimeter as the average of not less than six tests using standard benzoic acid.<sup>10</sup> These tests should be spaced over a period of not less than three days. Use not less than 0.9 g nor more than 1.1 g of standard benzoic acid (C<sub>6</sub>H<sub>5</sub>COOH). Make each determination according to the procedure described in Section 9 and compute the corrected temperature rise,  $t$ , as described in 10.1 or 10.2. Determine the corrections for nitric acid (HNO<sub>3</sub>) and firing wire as described in 10.3 and substitute in the following equation:

$$W = (Q \times g + e_1 + e_2)/t \quad (1)$$

where:

$W$  = energy equivalent of calorimeter, MJ/°C,

$Q$  = heat of combustion of standard benzoic acid, MJ/g, calculated from the certified value,

$g$  = weight of standard benzoic acid sample, g,

$t$  = corrected temperature rise, as calculated in 10.1 or 10.2, °C,

$e_1$  = correction for heat of formation of nitric acid, MJ, and

$e_2$  = correction for heat of combustion of firing wire, MJ.

8.1.1 Standardization tests should be repeated after changing any part of the calorimeter and occasionally as a check on both calorimeter and operating technique.

8.2 *Checking the Calorimeter for Use with Volatile Fuels*—Use 2,2,4-trimethylpentane to determine whether the results obtained agree with the certified value (47.788 MJ/kg, weight in air) within the repeatability of the test method. If results do not come within this range, the method of

<sup>8</sup> Cellophane tape Scotch Brand No. 600 or 610 available from the Minnesota Mining and Manufacturing Company meets the specification requirements.

<sup>9</sup> Obtainable from the National Bureau Standards, Washington, DC 20234, as standard sample No. 217b.

<sup>10</sup> See Jessup, R. S., "Precise Measurement of Heat of Combustion with a Bomb Calorimeter," NBS Monograph 7, U. S. Government Printing Office.

handling the sample may have to be changed (Annex A1.8). If this is not possible or does not correct the error, run a series of tests using 2,2,4-trimethylpentane to establish the energy equivalent for use with volatile fuels.

**8.3 Heat of Combustion of Pressure-Sensitive Tape or Gelatin/Mineral Oil**—Determine the heat of combustion of either the pressure-sensitive tape or 0.5 g gelatin capsule/mineral oil in accordance with Section 9 using about 1.2 g of tape or 0.5 g gelatin capsule/mineral oil and omitting the sample. Make at least three determinations and calculate the heat of combustion as follows:

$$Q_{\text{pst}} = (\Delta t \times W - e_1)/1000 \text{ a} \quad (2)$$

where:

$Q_{\text{pst}}$  = heat of combustion of the pressure-sensitive tape or mineral oil, MJ/kg,

$\Delta t$  = corrected temperature rise, as calculated in accordance with 10.1 or 10.2, °C,

$W$  = energy equivalent of the calorimeter, MJ/°C,

$e_1$  = correction for the heat of formation of  $\text{HNO}_3$ , MJ, and

$a$  = mass of the pressure-sensitive tape or gelatin capsule/mineral oil, g.

Average the determinations, and redetermine the heat of combustion of the tape or gelatin capsule/mineral oil whenever a new roll or batch is started.

## 9. Procedure

**9.1 Weight of Sample**—Control the weight of sample (including any auxiliary fuel) so that the temperature rise produced by its combustion will be equal to that of 0.9 to 1.1 g of benzoic acid (Note 6). Weigh the sample to the nearest 0.1 mg.

NOTE 6—If the approximate heat of combustion of the sample is known, the required weight can be estimated as follows:

$$g = 26.454/Q_s \quad (3)$$

where:

$g$  = weight of sample, g, and

$Q_s$  = MJ/kg.

NOTE 7—Some fuels may contain water and particulate matter (ash) that will degrade calorimetric values. If the heat of combustion is required on a clean fuel, filter the sample to remove free water and insoluble ash before testing.

**9.1.1** For highly volatile fluids, reduce loss with use of tape<sup>11</sup> or gelatin capsule mineral oil.

**9.1.2 Tape**—Place a piece of pressure-sensitive tape across the top of the cup, trim around the edge with a razor blade, and seal tightly. Place 3 by 12-mm strip of tape creased in the middle and sealed by one edge in the center of the tape disk to give a flap arrangement. Weigh the cup and tape. Remove from the balance with forceps. Fill a hypodermic syringe with the sample. The volume of sample can be estimated as follows:

$$V = (W \times 0.00032)/(Q \times D)$$

where:

$V$  = volume of sample to be used, mL,

$W$  = energy equivalent of calorimeter, J/°C,

$Q$  = approximate heat of combustion of the sample, MJ/kg, and

$D$  = density, kg/m<sup>3</sup>, of the sample.

**9.1.2.1** Add the sample to the cup by inserting the tip of the needle through the tape disk at a point so that the flap of tape will cover the puncture upon removal of the needle. Seal down the flap by pressing lightly with a metal spatula. Reweigh the cup with the tape and sample. Take care throughout the weighing and filling operation to avoid contacting the tape or cup with bare fingers. Place the cup in the curved electrode and arrange the fuse wire so that the central portion of the loop presses down on the center of the tape disk.

**9.1.3 Gelatin/Mineral Oil**—Weigh the cup and gelatin capsule. The capsule should only be handled with forceps. Add the sample to the capsule. Reweigh the cup with capsule and sample. If poor combustion is expected with the capsule, add several drops of mineral oil on the capsule and reweigh the cup and contents. Place the cup in the curved electrode and arrange the fuse wire so that the central portion of the loop contacts the capsule and oil.

**9.2 Water in Bomb**—Add 1.0 mL of water to the bomb from a pipet.

**9.3 Oxygen**—With the test sample and fuse in place, slowly charge the bomb with oxygen to 30-atm (3.0-MPa) gage pressure at room temperature (Note 9). Do not purge the bomb to remove entrapped air.

NOTE 8: Caution—Be careful not to overcharge the bomb. If, by accident, the oxygen introduced into the bomb should exceed 4.0 MPa, do not proceed with the combustion. An explosion might occur with possible violent rupture of the bomb. Detach the filling connection and exhaust the bomb in the usual manner. Discard the sample, unless it has lost no weight, as shown by reweighing.

NOTE 9—Lower or higher initial oxygen pressures may be used within the range from 2.5 to 3.5 MPa, provided the same pressure is used for all tests, including standardization.

**9.4 Calorimeter Water**—Adjust the calorimeter water temperature before weighing as follows:

|                                  |                          |
|----------------------------------|--------------------------|
| Isothermal jacket method         | 1.6 to 2.0°C             |
|                                  | below jacket temperature |
| Adiabatic jacket method is (9.6) | 1.0 to 1.4°C             |
|                                  | below room temperature.  |

NOTE 10—This initial adjustment will ensure a final temperature slightly above that of the jacket for calorimeters having an energy equivalent of approximately 10.2 MJ/°C. Some operators prefer a lower initial temperature so that the final temperature is slightly below that of the jacket. This procedure is acceptable, provided it is used in all tests, including standardization.

**9.4.1** Use the same amount ( $\pm 0.5$  g) of distilled or deionized water in the calorimeter vessel for each test. The amount of water (2000 g is usual) can be most satisfactorily determined by weighing the calorimeter vessel and water together on a balance. The water may be measured volumetrically if it is measured always at the same temperature.

**9.5 Observations, Isothermal Jacket Method**—Assemble the calorimeter in the jacket and start the stirrer. Allow 5 min for attainment of equilibrium, then record the calorimeter temperatures (Note 11) at 1-min intervals for 5 min. Fire

<sup>11</sup> Acceptable procedures for handling volatile liquids include those described in the reports referenced at the end of this test method. References (1) to (6) describe glass sample holders; (7) describes a metal sample holder; (8) describes a gelatin sample holder.

the charge at the start of the sixth minute and record the time and temperature,  $t_f$ . Add to this temperature 60 % of the expected temperature rise, and record the time at which the 60 % point is reached (Note 12). After the rapid rise period (about 4 to 5 min), record temperatures at 1-min intervals on the minute until the difference between successive readings has been constant for 5 min.

NOTE 11—Use a magnifier and estimate all readings (except those during the rapid rise period) to the nearest 0.002°C when using ASTM Bomb Calorimeter Thermometer 56C. Estimate Beckmann thermometer readings to the nearest 0.001°C and 25-Ω resistance thermometer readings to the nearest 0.0001 Ω. Tap mercurial thermometers with a pencil just before reading to avoid errors caused by mercury sticking to the walls of the capillary.

NOTE 12—When the approximate expected rise is unknown, the time at which the temperature reaches 60 % of the total can be determined by recording temperatures at 45, 60, 75, 90, and 105 s after firing and interpolating.

**9.6 Observations, Adiabatic Jacket Method (NOTE 13)—** Assemble the calorimeter in the jacket and start the stirrers. Adjust the jacket temperature to be equal to or slightly lower than the calorimeter, and run for 5 min to obtain equilibrium. Adjust the jacket temperature to match the calorimeter within ±0.01°C and hold for 3 min. Record the initial temperature (Note 6) and fire the charge. Adjust the jacket temperature to match that of the calorimeter during the period of rise, keeping the two temperatures as nearly equal as possible during the rapid rise, and adjusting to within ±0.01°C when approaching the final equilibrium temperature. Take calorimeter readings at 1-min intervals until the same temperature is observed in three successive readings. Record this as the final temperature. Time intervals are not recorded as they are not critical in the adiabatic method.

NOTE 13—These instructions supersede the instructions given in 9.5 when using jackets equipped for adiabatic temperature control.

**9.7 Analysis of Bomb Contents—** Remove the bomb and release the pressure at a uniform rate such that the operation will require not less than 1 min. Examine the bomb interior for evidence of incomplete combustion. Discard the test if unburned sample or sooty deposits are found.

**9.7.1** Wash the interior of the bomb, including the electrodes and sample holder, with a fine jet of water and quantitatively collect the washings in a beaker. Use a minimum of wash water, preferably less than 350 mL. Titrate the washings with standard alkali solution, using methyl orange or methyl red indicator.

**9.7.2** Remove and measure the combined pieces of unburned firing wire, and subtract from the original length. Record the difference as "wire consumed."

**9.7.3** Determine the sulfur content of the sample if it exceeds 0.1 %. Determine sulfur by analyzing the bomb washings remaining after the acid titration, using the procedure described in Test Method D 129.

## 10. Calculation

**10.1 Temperature Rise in Isothermal Jacket Calorimeter—** Using data obtained as prescribed in 9.5, compute the temperature rise,  $t$ , in an isothermal jacket calorimeter as follows:

$$t = t_c - t_a - r_1(b - a) - r_2(c - b) \quad (4)$$

where:

- $t$  = corrected temperature rise,
- $a$  = time of firing,
- $b$  = time (to nearest 0.1 min) when the temperature rise reaches 60 % of total,
- $c$  = time at beginning of period in which the rate of temperature change with time has become constant (after combustion),
- $t_a$  = temperature at time of firing, corrected for thermometer error (Note 14),
- $t_c$  = temperature at time,  $c$ , corrected for thermometer error (Note 14),
- $r_1$  = rate (temperature units per minute) at which temperature was rising during 5-min period before firing, and
- $r_2$  = rate (temperature units per minute) at which temperature was rising during the 5-min period after time  $c$ . If the temperature is falling,  $r_2$  is negative and the quantity  $-r_2(c - b)$  is positive.

NOTE 14—All mercury-in-glass thermometers must be corrected for scale error, using data from the thermometer certificate prescribed in Annex A1, A1.5.1, or A1.5.2. Beckmann thermometers also require a setting correction and an emergent stem correction (Annex A2, A2.1.2). Solid-stem ASTM Thermometers 56F and 56C do not require emergent stem corrections if all tests, including standardization are performed within the same 5.5°C interval. If operating temperatures exceed this limit, a differential emergent stem correction (Annex A2, A2.1.1) must be applied to the correct temperature rise,  $t$ , in all tests, including standardization.

**10.2 Temperature Rise in Adiabatic Jacket Calorimeter—** Using data obtained as prescribed in 9.6, compute the temperature rise,  $t$ , in an adiabatic jacket calorimeter as follows:

$$t = t_f - t_a \quad (5)$$

where:

- $t$  = corrected temperature rise,
- $t_a$  = temperature when charge was fired, corrected for thermometer error (Note 14, and
- $t_f$  = final equilibrium temperature, corrected for the thermometer error (Note 14).

**10.3 Thermochemical Corrections (Annex A2)—** Compute the following for each test:

- $e_1$  = correction for heat of formation of nitric acid (HNO<sub>3</sub>), MJ = cm<sup>3</sup> of standard (0.0866 N) NaOH solution used in titration × 5/10<sup>6</sup>,
- $e_2$  = correction for heat of formation of sulfuric acid (H<sub>2</sub>SO<sub>4</sub>), MJ = 58.6 × percentage of sulfur in sample × mass of sample/10<sup>6</sup>,
- $e_3$  = correction for heat of combustion of firing wire, MJ, = 1.13 × millimetres of iron wire consumed/10<sup>6</sup>, = 0.96 × millimetres of Chromel C wire consumed/10<sup>6</sup>, and
- $e_4$  = correction for heat of combustion of pressure-sensitive tape or gelatin capsule and mineral oil, MJ = mass of tape or capsule oil,  $g$  × heat of combustion of tape or capsule/oil, MJ/kg/10<sup>6</sup>.

**10.4 Gross Heat of Combustion—** Compute the gross heat of combustion by substituting in the following equation:

$$Q_g = (HV - e_1 - e_2 - e_3 - e_4)/1000 \text{ g} \quad (6)$$

where:

- $Q_g$  = gross heat of combustion, at constant volume expressed as MJ/kg (Note 10),  
 $t$  = corrected temperature rise as calculated in 10.1 or 10.2, °C,  
 $W$  = energy equivalent of calorimeter, MJ/°C (Section 8),  
 $e_1, e_2, e_3, e_4$  = corrections as prescribed in 10.3, and  
 $g$  = weight of sample, g.

NOTE 15—The gross heat of combustion at constant pressure may be calculated as follows:

$$Q_{gp} = Q_g + 0.006145H$$

where:

$Q_{gp}$  = gross heat of combustion at constant pressure,

$\frac{\text{MJ}}{\text{kg}}$ , and

$H$  = hydrogen content, mass %.

#### 10.5 Net Heat of Combustion:

10.5.1 If the percentage of hydrogen,  $H$ , in the sample is known, the net heat of combustion may be calculated as follows:

$$Q_n = Q_g - 0.2122 \times H \quad (7)$$

where:

$Q_n$  = net heat of combustion at constant pressure, MJ/kg,

$Q_g$  = gross heat of combustion at constant volume, MJ/kg, and

$H$  = mass percent of hydrogen in the sample.

10.5.2 If the percentage of hydrogen in aviation gasoline and turbine fuel samples is not known, the net heat of combustion may be calculated as follows:<sup>12</sup>

$$Q_n = 10.025 + (0.7195)Q_g \quad (8)$$

where:

$Q_n$  = net heat of combustion at constant pressure, MJ/kg,

$Q_g$  = gross heat of combustion at constant volume, MJ/kg.

<sup>12</sup> Equation 8 is recommended only if the percentage of hydrogen is not known. It is based in Eq 7 and an empirical relation between  $H$  and the percentage of hydrogen in aviation gasolines and turbine fuels, developed from data by R. S. Jessup and C. S. Cragos, "Net Heat of Combustion of AN-F-28 Aviation Gasolines," Nat. Advisory Committee for Aeronautics, Technical Note No. 996, June 1945, and Joseph A. Coglian and Ralph S. Jessup, "Relation Between Net Heat of Combustion and Aniline-Gravity Product of Aircraft Fuels," Nat. Bureau of Standards Report 2348, March 1953.

## 11. Report

11.1 Net heat of combustion is the quantity required in practical applications. The net heat should be reported to the nearest 0.005 MJ/kg.

NOTE 16—Usually the gross heat of combustion is reported for fuel oils in preference to net heat of combustion.

11.2 To obtain the gross or net heat of combustion in cal (I.T.)/g or Btu/lb divide by the appropriate factor reporting to the nearest 0.5 cal/g or 1 Btu/lb.

$$Q_{\text{net}} \text{ lb} = (Q, \text{ MJ/kg})/0.002326$$

$$Q_{\text{net}} \text{ lb} = (Q, \text{ MJ/kg})/0.0041868$$

## 12. Precision and Bias<sup>13</sup>

12.1 Precision—The precision of this test method as obtained by statistical examination of interlaboratory test results is as follows:

12.1.1 Repeatability—The difference between successive test results obtained by the same operator with the same apparatus under constant operating conditions on identical test material, would in the long run, in the normal and correct operation of the test method, exceed the values shown in the following table only in one case in twenty.

Repeatability 0.13 MJ/kg

12.1.2 Reproducibility—The difference between two single and independent results, obtained by different operators working in different laboratories on identical test material, would in the long run, in the normal and correct operation of the test method, exceed the values shown in the following table only in one case in twenty.

Reproducibility 0.40 MJ/kg

12.2 Bias—No general statement is made on bias for the standard since comparison with accepted reference materials (covering the range of values expected when the method is used) is not available.

<sup>13</sup> The summary of cooperative test data from which these repeatability and reproducibility values were calculated was published for information as Appendix XII to the 1957 Report of Committee D-2 on Petroleum Products and Lubricants. The summary of test data was also published from 1958 to 1966, inclusive, as Appendix III to ASTM Method D 240. The data are now filed at ASTM Headquarters as Research Report No. RR D-2-38.

## ANNEXES

## (Mandatory Information)

## A1. APPARATUS FOR HEAT OF COMBUSTION TEST

**A1.1 Test Room**—The room in which the calorimeter is operated must be free from drafts and not subject to sudden temperature changes. The direct rays of the sun shall not strike the jacket or thermometers. Adequate facilities for lighting, heating, and ventilating shall be provided. Thermostatic control of room temperature, and controlled relative humidity are desirable.

**A1.2 Oxygen Bomb**—The oxygen bomb shall have an internal volume of  $350 \pm 50$  mL. All parts shall be constructed of materials which are not affected by the combustion process or products sufficiently to introduce measurable heat input or alteration of end products. If the bomb is lined with platinum or gold, all openings shall be sealed to prevent combustion products from reaching the base metal. The bomb must be designed so that all liquid combustion products can be completely recovered by washing the inner surfaces. There must be no gas leakage during a test. The bomb must be capable of withstanding a hydrostatic pressure test to a gage pressure of 3000 psi (20 MPa) at room temperature, without stressing any part beyond its elastic limit.<sup>14</sup>

**A1.3 Calorimeter**—The calorimeter (Note A1.1) vessel shall be made of metal (preferably copper or brass) with a tarnish-resistant coating, and with all outer surfaces highly polished. Its size shall be such that the bomb will be completely immersed in water when the calorimeter is assembled. It shall have a device for stirring the water thoroughly and at a uniform rate, but with minimum heat input. Continuous stirring for 10 min shall not raise the calorimeter temperature more than  $0.01^\circ\text{C}$  starting with identical temperatures in the calorimeter, room, and jacket. The immersed portion of the stirrer shall be coupled to the outside through a material of low heat conductivity.

**NOTE A1.1**—As used in this test method, the term "calorimeter" designates the bomb, the vessel with stirrer, and the water in which the bomb is immersed.

**A1.4 Jacket**—The calorimeter shall be completely enclosed within a stirred water jacket and supported so that its sides, top, and bottom are approximately 10 mm from the jacket wall. The jacket may be arranged so as to remain at substantially constant temperature, or with provision for rapidly adjusting the jacket temperature to equal that of the calorimeter for adiabatic operation. It must be constructed so that any water evaporating from the jacket will not condense on the calorimeter.<sup>14</sup>

**A1.4.1** A double-walled jacket with a dead-air insulation space may be substituted for the constant-temperature water jacket if the calorimeter is operated in a constant-temperature ( $\pm 2^\circ\text{F}$ ) ( $\pm 1^\circ\text{C}$ ) room. The same ambient conditions

must be maintained for all experiments, including standardization.

**A1.5 Thermometers**—Temperatures in the calorimeter and jacket shall be measured with the following thermometers or combinations thereof:

**A1.5.1 Etched Stem, Mercury-in-Glass, ASTM Bomb Calorimeter Thermometer** having a range from  $66$  to  $95^\circ\text{F}$  or  $19$  to  $35^\circ\text{C}$ ,  $18.9$  to  $25.1^\circ\text{C}$ , or  $23.9$  to  $30.1^\circ\text{C}$ , as specified, and conforming to the requirements for Thermometer 56F, 56C, 116C, or 117C, respectively, as prescribed in Specification E 1. Each of these thermometers shall have been tested for accuracy at intervals no larger than  $2.5^\circ\text{F}$  or  $2.0^\circ\text{C}$  over the entire graduated scale. Corrections shall be reported to  $0.005^\circ\text{F}$  or  $0.002^\circ\text{C}$ , respectively, for each test point.

**A1.5.2 Beckmann Differential Thermometer**, range  $6^\circ\text{C}$  reading upward as specified and conforming to the requirements for Thermometer 115C as prescribed in Specification E 1. Each of these thermometers shall be tested for accuracy at intervals no larger than  $1^\circ\text{C}$  over the entire graduated scale and corrections reported to  $0.001^\circ\text{C}$  for each test point.

**A1.5.3 Calorimetric Type Platinum Resistance Thermometer**,  $25\text{-}\Omega$ .

**A1.6 Thermometer Accessories**—A magnifier is required for reading mercury-in-glass thermometers to one tenth of the smallest scale division. This shall have a lens and holder designed so as not to introduce significant errors due to parallax.

**A1.6.1** A Wheatstone bridge and galvanometer capable of measuring resistance of  $0.0001\ \Omega$  are necessary for use with resistance thermometers.

**A1.7 Timing Device**—A watch or other timing device capable of measuring time to 1 s is required for use with the isothermal jacket calorimeter.

**A1.8 Sample Holder**—Nonvolatile samples shall be burned in an open crucible of platinum (preferred), quartz or acceptable base metal alloy. Base metal alloy crucibles are acceptable if after a few preliminary firings the weight does not change significantly between tests.

**A1.9 Firing Wire**—Use a 100-mm length of No. 34 B & S gage iron wire or Chromel C resistance wire. Shorter lengths may be used if the same length is employed in all tests, including standardization tests. Platinum wire may be used if the ignition energy is small and reproducible.

**A1.10 Firing Circuit**—A 6 to 16-V alternating or direct current is required for ignition purposes with an ammeter or pilot light in the circuit to indicate when current is flowing. A step-down transformer connected to a 115-V 50/60 Hz lighting circuit of storage batteries may be used.

**A1.2 Caution**—The ignition circuit switch shall be of the momentary contact type, normally open, except when held closed by the operator.

**A1.11 Oxygen Purifying Device**—Commercial oxygen produced from liquid air can generally be used without

<sup>14</sup> The apparatus available from Parr Instrument Co., 211 Fifty-Third St., Moline, IL 61265 has been satisfactory for this purpose.

purification. Oxygen prepared by electrolysis of water should not be used without purification, as it may contain enough hydrogen to affect results by 1 % or more. Combustible

impurities may be removed from oxygen by passing it over copper oxide (CuO) at about 500°C.

## A2. CORRECTIONS

### A2.1 THERMOMETER CORRECTIONS<sup>15</sup>

A2.1.1 The differential emergent stem correction for solid stem calorimetric thermometers (56F and 56C) may be computed from the following equation:

$$\text{Differential stem correction} = K(t_c - t_a)(t_a + t_c - L - T) \quad (\text{A2.1})$$

where:

$K$  = differential expansion coefficient of mercury in glass = 0.00016 for Celsius thermometers or 0.00009 for Fahrenheit thermometers.

$L$  = scale reading to which the thermometer was immersed,

$T$  = mean temperature of emergent stem,

$t_a$  = initial temperature reading, and

$t_c$  = final temperature reading.

A2.1.2 Differential emergent stem correction for a Beckmann thermometer immersed to the zero of the scale may be computed as follows:

$$\text{Differential stem correction} = K(t_c - t_a)(S + t_c + t_a - T) \quad (\text{A2.2})$$

where:

$S$  = "setting" (temperature at zero reading) of the thermometer.

$K$ ,  $T$ ,  $t_c$  and  $t_a$  as defined in A2.1.1.

A2.1.3 "Setting" correction for a Beckmann thermometer may be computed as follows:

$$\text{"Setting" correction} = \text{factor} \times (t_c - t_a)$$

where:

Factor is obtained from Table A2.1 and

$t_c$  and  $t_a$  as defined in A2.1.1.

### A2.2 THERMOCHEMICAL CORRECTIONS

A2.2.1 *Heat of Formation of Nitric Acid*—A correction of 5 J is applied for each cubic centimetre of standard (0.0866 N) or standard (0.0725 N) NaOH solution used in the acid titration. This is based on the assumption that (1) all of the

TABLE A2.1 Correction Factors

| Setting | Factor  |
|---------|---------|
| 15      | -0.0015 |
| 20      | 0.0000  |
| 25      | +0.0015 |
| 30      | +0.0029 |
| 35      | +0.0043 |
| 40      | +0.0056 |

acid titrated is HNO<sub>3</sub> and (2) the heat of formation of 0.1 N HNO<sub>3</sub> under the test conditions is 57.8 kJ/mole. When H<sub>2</sub>SO<sub>4</sub> is also present, part of the correction for H<sub>2</sub>SO<sub>4</sub> is contained in the  $e_1$  correction, and the remainder in the  $e_2$  correction.

A2.2.2 *Heat of Formation of Sulfuric Acid*—A correction of 5.86 kJ is applied to each gram of sulfur in the sample. This is based upon the heat of formation of 0.17 N H<sub>2</sub>SO<sub>4</sub>, which is -301.4 kJ/mole. But, a correction equal to  $2 \times 57.8$  kJ/mole of sulfur was applied for H<sub>2</sub>SO<sub>4</sub> in the  $e_1$  correction. Thus, the additional correction necessary is  $301.4 - (2 \times 57.8) = 185.8$  kJ/mole or 5.86 kJ/g of sulfur.

A2.2.2.1 The value of 5.86 kJ/g of sulfur is based on a fuel oil containing a relatively large amount of sulfur since as the percentage of sulfur decreases, the correction decreases and consequently a larger error can be tolerated. For this calculation 0.8 % S, 99.2 % CH<sub>2</sub> was taken as the empirical composition of fuel oil. If a 0.6-g sample of such a fuel oil is burned in a bomb containing 1 cm<sup>3</sup> of water, the H<sub>2</sub>SO<sub>4</sub> formed will be approximately 0.17 N.

A2.2.2.2 Using data from National Bureau of Standards Circular No. 500, the heat of reaction SO<sub>2</sub> (g) + 1/2 O<sub>2</sub> (g) + 651 H<sub>2</sub>O (l) - H<sub>2</sub>SO<sub>4</sub> · 650 H<sub>2</sub>O (l) at constant volume and 3 MPa is -301.4 kJ/mole.

A2.2.3 *Heat of Combustion of Fuse Wire*—The following heats of combustion are accepted:

|                                  |   |           |
|----------------------------------|---|-----------|
| Iron wire, No. 34 B & S gage     | = | 1.13 J/mm |
| Chromel C wire No. 34 B & S gage | = | 0.96 J/mm |

A2.2.4 *Heat of Combustion of Pressure-Sensitive Tape*—The correction for the heat of combustion of the tape (as determined in accordance with 8.3) assumes complete combustion of the tape.

## A3. PRECAUTIONARY STATEMENTS

### A3.1 Sodium Hydroxide

**Warning**—Corrosive. Can cause severe burns or blindness. Evolution of heat produces a violent reaction or eruption upon too rapid mixture with water.

Before using, secure information on procedures and protective measures for safe handling.

Do not get in eyes, on skin, on clothing.

Avoid breathing dusts or mists.

Do not take internally.

When handling, use chemical safety goggles or face shield, protective gloves, boots and clothing.

When mixing with water, add slowly to surface of solution to avoid violent splattering. In the preparation of solutions do not use hot water, limit temperature rise, with agitation, to 10°C/min or limit solution temperature to a maximum of 90°C. No single addition should cause a concentration increase greater than 5 %.

<sup>15</sup> For a complete discussion of those corrections see the American Institute of Physics Symposium, *Temperature, Its Measurement and Control in Science and Industry*, Reinhold Publishing Corp., New York, NY 1941.



### A3.2 Oxygen

- Warning—Oxygen vigorously accelerates combustion.  
Do not exceed the sample size limits.  
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 G-4.1 for details of safe practice in the use of oxygen.

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### A3.3 2,2,4-Trimethylpentane

- Warning—Extremely flammable. Harmful if inhaled.  
Vapors may cause flash fire.  
Keep away from heat, sparks, and open flame.  
Keep container closed.  
Use with adequate ventilation.  
Avoid buildup 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.

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ASTM E 537-86

Standard Test Method for Assessing the Thermal Stability  
Of Chemicals By Methods Of Differential Thermal Analysis



## Standard Test Method for Assessing The Thermal Stability Of Chemicals By Methods Of Differential Thermal Analysis<sup>1</sup>

This standard is issued under the fixed designation E 537; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

### INTRODUCTION

Committee E-27 is currently engaged in developing methods to determine the hazard potential of chemicals. An estimate of this potential may usually be obtained by using program CHETAH (ASTM D5 51) to compute the maximum energy of reaction of the chemical or mixture of chemicals.<sup>2</sup>

The expression "hazard potential" as used by this committee is defined as the degree of susceptibility of material to ignition or release of energy under varying environmental conditions.

The primary purpose of this test method is to detect enthalpic changes and to approximate the temperature of initiation of these events. Thermal analysis techniques including differential thermal analysis (DTA) and differential scanning calorimetry (DSC) offer the advantage of using very small samples on the order of a few milligrams. Revision of this test method has been undertaken to extend the assessment of thermal stability of chemicals through use of atmospheres at elevated pressure.

### 1. Scope

1.1 This test method covers the ascertainment of the presence of enthalpic changes, using a minimum quantity of sample, normally in the milligram range, and approximates the temperature at which these enthalpic changes occur.

1.2 This test method utilizes techniques of differential thermal analysis (DTA) and differential scanning calorimetry (DSC); it may be performed on solids, liquids, or slurries.

1.3 This test method may be carried out in an inert or a reactive atmosphere with an absolute pressure range from 100 Pa through 7 MPa and over a temperature range from -150°C to above 1000°C.

1.4 *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 the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use. Specific safety precautions are given in Section 8.*

### 2. Referenced Documents

#### 2.1 ASTM Standards:

E 472 Practice for Reporting Thermoanalytical Data<sup>3</sup>

E 473 Definitions of Terms Relating to Thermal Analysis<sup>3</sup>

E 967 Practice for Temperature Calibration of Differential Scanning Calorimeters and Differential Thermal Analyzers<sup>3</sup>

### 3. Terminology

#### 3.1 Definitions:

3.1.1 *differential thermal analysis (DTA)*—a technique in which the temperature difference between the substance and a reference material is measured as a function of temperature while the substance and reference material are subjected to a controlled temperature program (ITCA, 1980) (see Definitions E 473).

3.1.2 *differential scanning calorimetry (DSC)*—a technique in which the difference in energy inputs into a substance and a reference material is measured as a function of temperature while the substance and reference material are subjected to a controlled temperature program (ITCA, 1980) (see Definitions E 473).

#### 3.2 Descriptions of Terms Specific to This Standard:

3.2.1 *DTA (DSC) curve*—a record of a thermal analysis where the temperature difference ( $\Delta T$ ) or the energy change ( $\Delta q$ ) is plotted on the ordinate and temperature or time is plotted on the abscissa (see Figs. 1 and 2 and Definitions E 473).

3.2.2 *peak*—that portion of a heating curve which is attributable to the occurrence of a single process. It is normally characterized by a deviation from the established baseline, a maximum deflection, and a reestablishment of a baseline not necessarily identical to that before the peak (see Fig. 1).

NOTE 1—There will be instances when upon scanning in temperature an endotherm will be observed that is immediately followed by or is

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee E-27 on Hazard Potential of Chemicals and is the direct responsibility of Subcommittee E27.02 on Thermal Stability.

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<sup>2</sup> A complete assessment of the hazard potential of chemicals must take into account a number of realistic factors not considered in this test method or the CHETAH program.

<sup>3</sup> *Annual Book of ASTM Standards*, Vol 14.02.

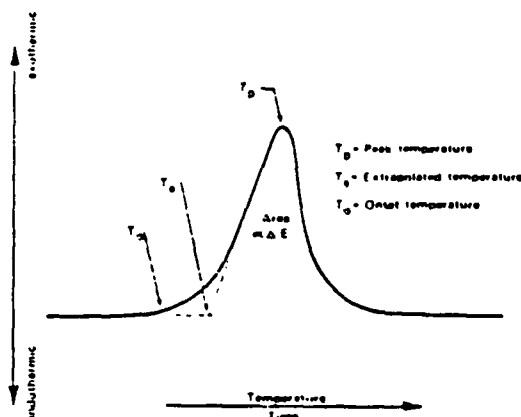


FIG. 1 Typical DTA—DSC Curve with Exotherm

in conjunction with an exotherm as shown in Fig. 2. This type of competing reactions makes it difficult and at times impossible to locate the true peak and onset temperatures.

**3.2.3 peak temperature**—the temperature corresponding to the maximum deflection of the DTA or DSC curve.

**3.2.4 onset temperature**—the temperature at which a deflection from the established baseline is first observed.

**3.2.5 extrapolated onset temperature**—empirically, the temperature found by extrapolating the baseline (prior to the peak) and the leading side of the peak to their intersection (see Fig. 1).

**3.2.6 reaction**—any transformation of material accompanied by a change of enthalpy which may be endothermic or exothermic.

**3.2.7 thermal stability**—the absence of a reaction (for the purposes of this test method only, see 3.2.6).

#### 4. Summary of Method

**4.1** In DTA, thermocouples for both the sample and reference material are connected in series-opposition so as to measure a temperature difference ( $\Delta T$ ). An additional thermocouple is provided to measure the absolute temperature ( $T$ ) of the sample or reference.

**4.2** In DSC, a measurement is made of the energy change ( $\Delta q$ ) associated with the observed change of enthalpy. Provisions are made to measure the absolute temperature ( $T$ ) of the sample or reference or the average temperature of both.

**4.3** A sample of the material to be examined and of a thermally inert reference material are placed in separate holders.

**4.4** The sample and reference materials are simultaneously heated at a controlled rate of up to 30°C/min under an equilibrated atmosphere. A record of  $\Delta T$  or  $\Delta q$  is made as a function of temperature ( $T$ ). Alternatively, the temperature of the sample and reference may be increased to a fixed and predetermined value and a record of  $\Delta T$  or  $\Delta q$  made as a function of time ( $t$ ).

**4.5** When the sample undergoes a transition involving a change of enthalpy, that change is indicated by a departure

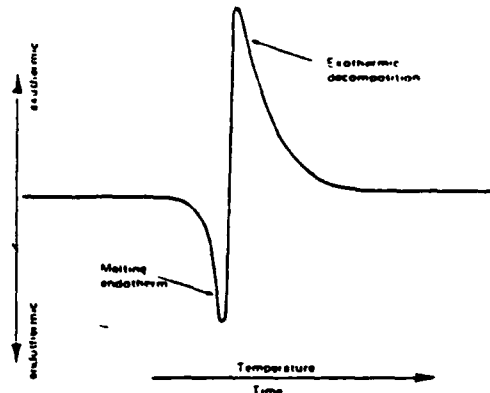


FIG. 2 Thermogram Illustrating a Melting Process Immediately Followed by an Exothermic Decomposition

from the initially established baseline of the temperature record.

#### 5. Significance and Use

**5.1** This test method is useful in detecting potentially hazardous reactions including those from volatile chemicals and in estimating the temperatures at which these reactions occur. This test method is recommended as an early test for detecting the reactive hazards of an uncharacterized chemical substance or mixture (note Section 8).

**5.2** The magnitude of change of enthalpy may not necessarily denote the relative hazard. For example, certain exothermic reactions are often accompanied by gas evolution which increases the potential hazard. Alternatively, the extent of energy release for certain exothermic reactions may differ widely with the extent of confinement of volatile products. Thus, the presence of an exotherm or of an endotherm and its approximate temperature are the most significant criteria in this test method (see Section 3 and Fig. 1).

**5.3** When volatile substances are being studied, it is important to perform this test with a confining pressurized atmosphere so that changes of enthalpy which can occur above normal boiling or sublimation points may be detected. As an example, an absolute pressure of 1.14 MPa (150 psig) will generally elevate the boiling point of a volatile organic substance 100°C. Under these conditions exothermic decomposition is often observed.

**5.4** For some substances the rate of enthalpy change during an exothermic reaction may be small at normal atmospheric pressure, making an assessment of the temperature of instability difficult. Generally a repeated analysis at an elevated pressure will improve the assessment by increasing the rate of change of enthalpy.

**5.5** Although certain types of thermal analysis instrumentation offer the additional advantage of measuring the magnitude of the change in enthalpy, such measurements are beyond the scope of this test method. The three significant criteria of this test method are: the detection of a change of enthalpy; the approximate temperature at which the event occurs; and the observance of effects due to the cell atmosphere and pressure.

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## 6. Limitations

6.1 A host of environmental factors affect the existence, magnitude, and temperature of an exothermic reaction. Some, including heating rate, instrument sensitivity, degree of confinement, and atmosphere reactivity will affect the detectability of an exothermic reaction using this procedure. Therefore, it is imperative that the qualitative results obtained from the application of this test method be viewed only as an indication of the thermal stability of a chemical.

## 7. Apparatus

7.1 The equipment used in this test method shall be capable of displaying changes of enthalpy as a function of either time ( $t$ ) or temperature ( $T$ ), and shall have the capability of subjecting the sample cell to different atmospheres of equilibrated pressures.

7.2 The differential thermal analytical instrument (DTA or DSC) may be purchased or custom built to various degrees of refinement and sophistication. The basic components of an apparatus satisfactory for this test method include:

7.2.1 Sample containers,

7.2.2 Measuring cell capable of containing a pressure of 7 MPa,

7.2.3 Heating unit,

7.2.4 Programmable temperature controller,

7.2.5 Continuous temperature measuring and recording equipment, and

7.2.6 Stable, adjustable pressure supply.

7.3 Analysis may be initiated at a temperature below ambient by providing a means of cooling the sample and reference, their respective containers, and the heating unit to the same initial temperature.

## 8. Safety Precautions

8.1 The use of this test method as an initial test for material whose potential hazards are unknown requires that precautions be taken during the sample preparation and testing.

8.2 Where particle size reduction by grinding is necessary, the user of the test method should presume that the material is dangerous.

8.3 The use of this test method may require operation at elevated temperatures and pressures. All precautions associated with such temperatures and pressures should be observed.

## 9. Calibration

9.1 For purposes of this test method, calibrate the absolute temperature scale within  $\pm 2^\circ\text{C}$  in accordance with Practice E 967.

## 10. Sample and Reference Materials

10.1 The selection of an adequate sample size will depend upon the availability of the material, the degree of dilution required, the sensitivity of the instrument, the magnitude of the change of enthalpy, and the heating rate. Additionally, sample size must be compatible with the potential for a sudden large energy release. This test method should, therefore, be carried out on as small a quantity of material as possible, typically 1 to 50 mg.

10.2 Samples should be representative of the material being studied including particle size and purity.

10.3 The reference material must not undergo any thermal transformation over the temperature range under study. Typical reference materials include calcined aluminum oxide, glass beads, silicone oil, or an empty container.

10.4 Samples shall be prepared to achieve good thermal contact between them and their containers. For liquid samples it is recommended that approximately 20 % by weight of an inert material like aluminum oxide be added to the sample.

## 11. Recommended Conditions of Tests

11.1 *Sample Size*—A 5-mg sample is generally considered adequate. Decrease the sample size if the response is too energetic.

11.2 *Heating Rate*—A rate of 10 to  $30^\circ\text{C}/\text{min}$  is considered normal. If an endothermic response is immediately followed by an exotherm (Note 1, Fig. 2), then lower heating rates of 2 to  $10^\circ\text{C}/\text{min}$  are recommended.

11.3 *Temperature Range*—The temperature shall range from room temperature to  $500^\circ\text{C}$ .

11.4 *Pressure Range*—An equilibrated absolute pressure of 1.14 MPa (150 psig) is adequate for most elevated pressure tests.

11.5 *Y-Axis Sensitivity*—The equivalence of  $1\text{ m W}/\text{cm}$  is usually sufficient to record the entire exotherm. Decreases in y-axis sensitivity may be necessary if the reaction is too energetic.

## 12. Procedure

12.1 Prepare a sample of the material to be examined and of the reference material in respective containers and place into the measuring cell. Be certain intimate thermal contact with the sensors is achieved. (See 10.1 for appropriate sample size.)

NOTE 2—For volatile materials it is often of interest to examine thermal stability at temperatures beyond the normal boiling or sublimation point. Additionally, samples suspect of being potentially energetic may exhibit nondescript exothermic activity at ambient pressure. In either situation a repeat analysis in an atmosphere of elevated pressure using either sealed sample containers or a pressurized measuring cell is recommended.

12.2 For equipment that includes a pressurizable measuring cell, seal and adjust the measuring cell atmosphere to the desired equilibrium pressure. An absolute pressure of 1.14 MPa is recommended for an elevated pressure thermal analysis of organic substances using this test method.

NOTE 3—When sealed containers are used, they should be provided with a vent (pinhole) to ensure that the internal pressure is in equilibrium with the applied pressure.

12.3 For equipment that cannot maintain an elevated pressure within its measuring cell, place the sample and reference materials in hermetically sealed containers with an appropriate atmosphere.

NOTE 4—Hermetically sealed containers will self-pressurize due to increased partial pressures with increasing temperature. For most samples, however, this internal pressure will not be known but is typically less than 300 kPa. This approach is, therefore, a less satisfactory alternative for elevated pressure thermal analysis than a pressurized cell.

12.4 Heat the measuring cell at a controlled rate of up to 30°C/min and record the DTA or DSC curve. Continue heating until the highest temperature of interest is recorded or until the sample is destroyed or is lost by volatilization. For most organic compounds the normal temperature range is from 20 to 500°C.

NOTE 5—Any increase in heating rate may accentuate the recorder response for the ordinate but will also increase the measured onset temperature of an exothermic reaction.

12.5 Restore the measuring cell to ambient temperature and pressure upon completion of the analysis.

12.6 It may be informative to repeat the analysis at a slower heating rate (2°C/min to 10°C/min) when a complex change of enthalpy is encountered (see Fig. 2 and Note 1).

### 13. Report

13.1 Reporting of thermal data generated with this test method should comply with that outlined in Practice E 472 including a complete description of:

13.1.1 Sample and reference by name, composition, combination thereof, or formula, or

13.1.2 Apparatus and sample containers.

13.1.3 Composition and pressure of the sample atmosphere.

13.1.4 Heating rate and temperature range, and

13.1.5 Y-axis sensitivity.

13.2 Determine the onset, extrapolated onset, and peak temperatures of all reactions recorded from the DTA (DSC) curve.

13.3 When a thermal analysis is repeated using a different atmospheric composition or pressure or a different heating rate, note any significant changes in the DTA (DSC) curves resulting from the different experimental conditions. The magnitude of the recorded change of enthalpy, if measurable, may be significant but is beyond the scope of this test method.

### 14. Precision and Bias

14.1 The object of this test method is to ascertain the presence or absence of an exotherm and the approximate temperature of onset. Neither the magnitude of the exotherm nor the absolute value of the onset temperature are critical to the test method.

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APPENDIX C  
CALCULATIONS FOR TABLE 12



Given information:

|                           |  |
|---------------------------|--|
| <u>No. 2 Fuel Oil</u>     | Delta H = 19500 Btu/lb<br>Density = 7.22 lb/gal<br>Cost = \$0.104/lb   |
| <u>Acetone</u>            | Delta H = 13229 Btu/lb<br>Density = 6.68 lb/gal<br>Cost = \$0.30/lb <sup>a</sup>   |
| <u>Nitrocellulose(NC)</u> | Delta H = 4100 Btu/lb<br>Density = 11.68 lb/gal<br>Storage cost = \$0.47/lb <sup>b</sup><br>Incineration cost = \$0.09/lb <sup>b</sup> |

Calculations:

1. Dilution ratio = volume of diluent/volume of solvent

where diluent = No. 2 fuel oil  
solvent = acetone

2. Weight percentages of the No. 2 fuel oil, acetone, and NC mixture

Given: 1) Final NC concentration (fraction<sub>NC</sub>)  
2) Dilution ratio  
3) Arbitrary volume of acetone (in gallons)  
4) NOTE: For a given NC concentration and dilution ratio, the weight percentages will be the same regardless of the initial volume of acetone specified.

Arbitrary gallons of fuel oil = dilution ratio \* gallons of acetone  
Arbitrary lbs of fuel oil = gallons of fuel oil \* density<sub>fuel oil</sub>  
Arbitrary lbs of acetone = gallons of acetone \* density<sub>acetone</sub>  
Arbitrary lbs of total mixture = (lbs of fuel oil + lbs of acetone) / (1 - fraction<sub>NC</sub>)  
Arbitrary lbs of NC = lbs of mixture \* fraction<sub>NC</sub>

% NC = fraction<sub>NC</sub> \* 100%

% No. 2 fuel oil = (lbs of fuel oil/lbs of mixture) \* 100%

% Acetone = (lbs of acetone/lbs of mixture) \* 100%

Fraction<sub>fuel oil</sub> = % fuel oil/100%

Fraction<sub>acetone</sub> = % acetone/100%

3. Heat of combustion for mixture (delta H<sub>mixture</sub>) =  
(delta H<sub>fuel oil</sub> \* fraction<sub>fuel oil</sub>) + (delta H<sub>acetone</sub> \* fraction<sub>acetone</sub>) + (delta H<sub>NC</sub> \* fraction<sub>NC</sub>)

4. Mixture input (lb/hr) = boiler size/delta  $H_{\text{mixture}}$

$$\text{Mixture input (gpm)}^c = (\text{Lbs of fuel oil/density}_{\text{fuel oil}} + \text{lbs of acetone/density}_{\text{acetone}} + \text{lbs of NC/density}_{\text{NC}})/60$$

where lbs of fuel oil = fraction<sub>fuel oil</sub> \* mixture input (lb/hr)

lbs of acetone = fraction<sub>acetone</sub> \* mixture input (lb/hr)

lbs of NC = fraction<sub>NC</sub> \* mixture input (lb/hr)

5. Cost to burn mixture = (lbs of fuel oil \* cost<sub>fuel oil</sub>) +  
(lbs of acetone \* cost<sub>acetone</sub>) - (lbs of NC \* (storage cost<sub>NC</sub>  
+ incineration cost<sub>NC</sub>)) - (lbs of fuel oil saved \* cost<sub>fuel oil</sub>)

where lbs of fuel oil saved (for given boiler size) =

lbs of fuel oil only required - lbs fuel oil in mixture =

(boiler size/delta  $H_{\text{fuel oil}}$ ) - (fraction<sub>fuel oil</sub> \*  
mixture input (lb/hr))

6. Cost to burn No. 2 fuel oil only =  
((boiler size/delta  $H_{\text{fuel oil}}$ ) \* cost<sub>fuel oil</sub>)

7. Cost to burn mixture over No. 2 fuel oil only =  
cost to burn mixture - cost to burn fuel oil only

8. Amount of NC consumed = lbs of NC \* 3.973

where 3.973 = conversion from lb/hr to metric tons/yr  
using 24 hr/day and 365 days/yr

<sup>a</sup>Cost data taken from Chemical Marketing Reporter, December 1, 1989.

<sup>b</sup>Cost data taken from "Utilization of Energetic Materials in an  
Industrial Combustor", Oak Ridge National Laboratory, June 30, 1985.

<sup>c</sup>Gpm = gallons per minute.

APPENDIX D  
CALCULATIONS FOR TABLE 13

Given information:

No. 2 Fuel oil

Delta H = 19500 Btu/lb  
Density = 7.22 lb/gal  
Cost = \$0.104/lb

Nitrocellulose (NC)

Delta H = 4100 Btu/lb  
Density = 11.68 lb/gal  
Storage cost = \$0.47/lb<sup>a</sup>  
Incineration cost = \$0.09/lb<sup>a</sup>

1. Fractions of No. 2 fuel oil and NC

Fraction<sub>NC</sub> = Arbitrarily chosen (0.0 to 1.0)  
Fraction<sub>fuel oil</sub> = 1.0 - fraction<sub>NC</sub>

2. Heat of combustion for mixture (delta H<sub>mixture</sub>) =  
(delta H<sub>fuel oil</sub> \* fraction<sub>fuel oil</sub>) +  
(delta H<sub>NC</sub> \* fraction<sub>NC</sub>)

3. Mixture input (lb/hr) = boiler size/delta H<sub>mixture</sub>

Mixture input (gpm)<sup>b</sup> = (lbs of fuel oil/density<sub>fuel oil</sub> +  
lbs of NC/density<sub>NC</sub>)/60

where lbs of fuel oil = fraction<sub>fuel oil</sub> \* mixture input (lb/hr)  
lbs of NC = fraction<sub>NC</sub> \* mixture input (lb/hr)

4. Cost to burn mixture = (lbs of fuel oil \* cost<sub>fuel oil</sub>) -  
(lbs of NC \* (storage cost<sub>NC</sub> + incineration cost<sub>NC</sub>)) -  
(lbs of fuel oil saved \* cost<sub>fuel oil</sub>)

where lbs of fuel oil saved (for given boiler size) =  
lbs of fuel oil only required - lbs fuel oil in mixture =  
(boiler size/delta H<sub>fuel oil</sub>) - (fraction<sub>fuel oil</sub> \*  
mixture input (lb/hr))

5. Cost to burn No. 2 fuel oil only = (boiler size/delta H<sub>fuel oil</sub>) \* cost<sub>fuel oil</sub>

6. Cost to burn mixture over No. 2 fuel oil only =  
cost to burn mixture - cost to burn fuel oil only

7. Amount of NC consumed = lbs of NC \* 3.973

where 3.973 = conversion from lb/hr to metric tons/hr  
using 24 hr/day and 365 days/yr

<sup>a</sup>Cost data from "Utilization of Energetic Materials in an Industrial Combustor", Oak Ridge National Laboratory, June 30, 1985.

<sup>b</sup>Gpm = gallons per minute.