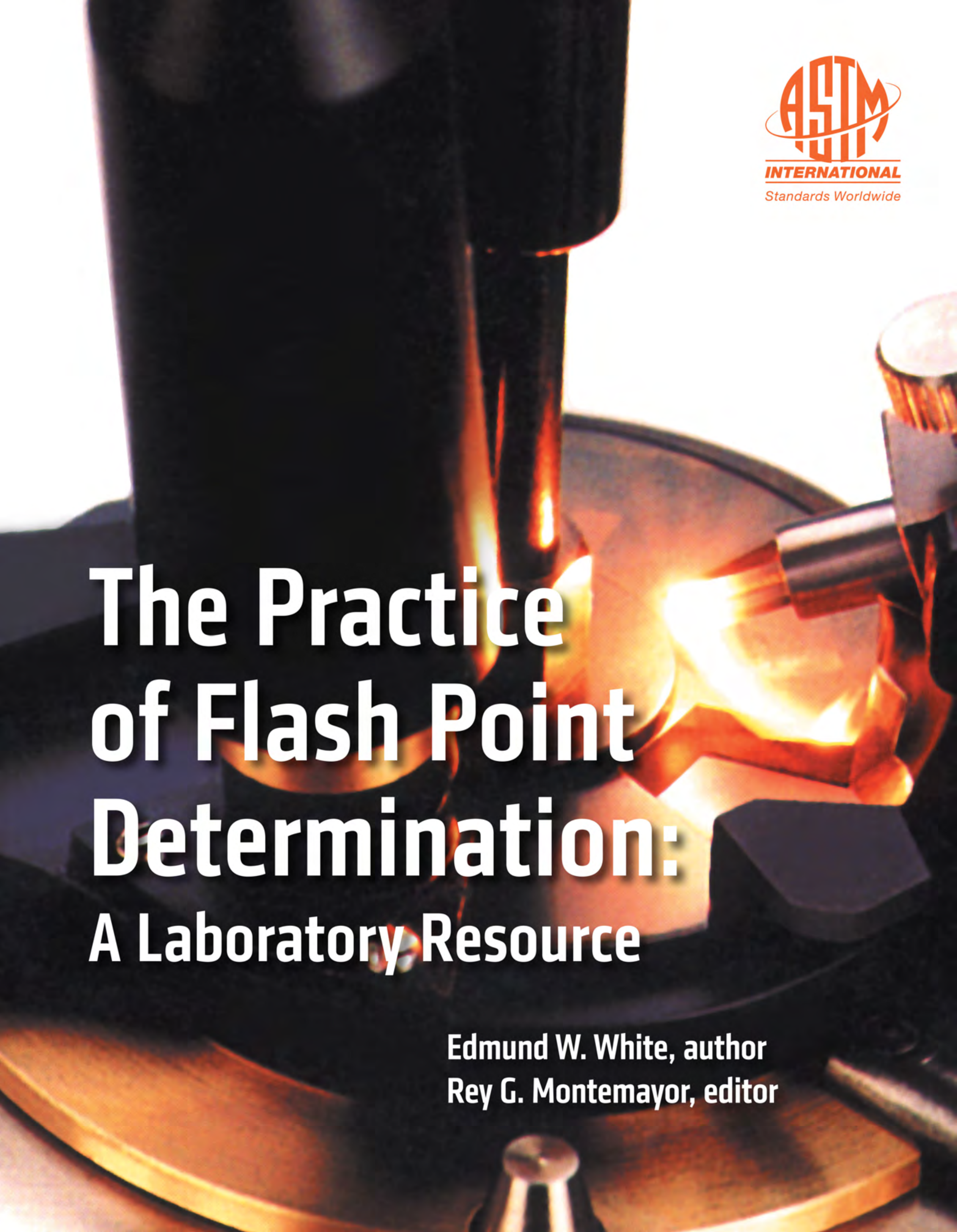

INTERNATIONAL

Standards Worldwide

The Practice of Flash Point Determination:

A Laboratory Resource

Edmund W. White, author

Rey G. Montemayor, editor

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Foreword

This manual is sponsored by the Flammability Section of ASTM Subcommittee D02.08 of ASTM Committee D02 on Petroleum Products and Lubricants. Ed White volunteered to write the manual and with the help, advice, and input of a Technical Advisory and Resource Group (TARG), comprised of individuals knowledgeable in flash point determination. TARG consisted of Bud Nesvig, Michael Collier, Michael Sherratt, Susan Litka, Didier Pigeon, Roland Ashauer, Katsuhiko Shimodaira, Thomas Herold, Volkmar Wierzbicki, Len Wachel, Michael Palmer, Alex Lau, and Rey Montemayor. Sincere acknowledgment and gratitude are due to these individuals for making possible the publication of this manual.

Unfortunately, before the peer review process was completed, Ed passed away unexpectedly. Kathy Dernoga of the ASTM books and journals staff asked me to revise the manuscript to address recommendations from the reviewers and put the final touches on the manuscript. Special thanks are due to Kathy Dernoga and Monica Siperko who provided needed help in the publication process.

I am certain that Ed would like to acknowledge and give thanks to his wife, Natalie, for her support and encouragement while writing the manual. It is unfortunate that Ed would not see the fruit of his tremendous effort. We owe Ed White a lot, and hopefully his intent in writing the manual is realized.

Rey G. Montemayor, Ph.D.
September 25, 2012

Contents

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Introduction

GENERAL

The concept of flash point was developed in the mid-nineteenth century in response to a spate of fires resulting from the sale of contaminated kerosine or the mishandling of combustible liquids. Flash point is the lowest temperature of a liquid at which sufficient vapor is generated to create a flammable mixture with air in the presence of an ignition source. Thus, in comparing two combustible liquids, the one with the lower flash point would tend to be the one that is more likely to form a flammable concentration in air and is thus considered the more dangerous of the two. Because the actual flash point is dependent upon the apparatus and procedure used in its measurement, liquids to be compared must be evaluated using the same apparatus and procedure. This manual will compare commonly used flash point apparatus and procedures in current use and will provide general guidance in the use and interpretation of standard flash point methods.

A BIT OF HISTORY [1–3]

As the middle of the nineteenth century approached, mankind had been dependent for many millennia on the combustion of natural products to provide light during the night hours. Candles made from a variety of natural waxes and wick lamps burning various animal and vegetable oils, fats, and greases had evolved. By the seventeenth century, the Betty lamp, consisting of a metal bowl containing oil (such as fish oil) and of a wick lying in a slot and protruding from the side of the bowl, was in common use.

Many of the natural fats and oils tended to produce smoky flames with little illumination. The whaling industry had developed in part from the search for better illuminating oils and improved lubricants. Among the variety of whales, the sperm whale was found to yield a superior illuminating oil, and the spermaceti from sperm whale heads was found to make the finest candles. Around 1851, in Scotland, James Young began to market an even better illuminant, a coal oil distilled from a liquid by-product from the coking of bituminous coal. However, the success of this illuminant was short lived because the production of crude petroleum (which, in the United States, began with the discovery well of Edwin Drake in western Pennsylvania in 1859) made available an abundant, inexpensive illuminant of high lighting efficiency. This product was known as kerosine, but the name "coal oil" lived on for many years as a synonym for the new product.

In ancient times, crude oil from natural seeps had been used as a medicine, lubricant, and lamp oil. It had also been a major ingredient in the so-called "Greek fire," an incendiary material used in ancient and medieval warfare [1,3,4]. Furthermore, Drake's well was not the first drilled to produce oil. For example, there are reports of the Chinese finding oil when drilling for salt in the third century AD Such wells are said to have reached a depth of 3,000 feet by the twelfth century. Marco Polo reported commercial production in Baku when he passed through northern Persia in the middle of the thirteenth century. Moreover, a product similar to kerosine had been in use for over a thousand years, and Tsar Peter the Great of Russia is said to have ordered a supply of "white oil" in 1723. Nevertheless, it was Drake's well and the subsequent boom in oil production that introduced the modern era of oil production and refining.

In the United States, the advent of kerosine brought with it a creative outpouring of lamp improvements that resulted in an average of 80 patents a year during the 20 years following the drilling of the Drake well [1]. The patents were granted for improved oil lamps, that is, for technical improvements, but there were also a number of improvements to make the lamps more attractive to the housekeeper. Although city homes gradually converted their lighting systems, first to city gas and then to electricity, the kerosine lamp with a flat wick, a perforated metallic oil container, and a plain glass chimney was used extensively in rural areas until the advent of rural electrification programs during the Roosevelt era of the 1930s.

KEROSINE

The terms "kerosine" and "kerosine distillate" have been used generally to mean any distillate fraction from petroleum, shale oil, or coal with an approximate boiling range of 150–300°C (302–572°F). Modern-day kerosine is defined in the American Society for Testing and Materials (ASTM) D3699 Standard Specification for Kerosine as "a refined petroleum distillate consisting of a homogeneous mixture of hydrocarbons essentially free of water, inorganic acidic or basic compounds, and excessive amounts of particulate contaminants." Furthermore, this specification establishes two grades of kerosine. Grade No. 1-K is a special low-sulfur grade (0.04 % sulfur maximum) suitable for kerosine burning appliances not connected to flues and for use in wick-fed illuminating lamps. Grade No. 2-K is a regular grade (0.30 % sulfur maximum) suitable for use in flue-connected burner appliances and for use in wick-fed illuminating lamps. No initial boiling point is specified for either grade, but a 10 % volume recovered temperature determined by ASTM Test Method D86 is limited to a maximum of 205°C (401°F) and the end point remains 300°C for both grades.

Other than the sulfur limits, the detailed requirements of the two grades are identical. For example, in addition to several other requirements, both are limited to the viscosity range of 1.0 to 1.9 mm^2/s (cSt); both are limited to a maximum freezing point temperature of −30°C; and both are limited to a minimum Saybolt color of +16. In ASTM Test Method Dl56 for Saybolt Color of Petroleum Products (Saybolt Chromometer Method), a +30 designates the lightest color and a −16 designates the darkest color.

Today's kerosine is thus a closely defined product. It is made in high-technology refineries using sophisticated instrumentation and computer-controlled processes, and quality is ensured by either on-stream analyzers or quality control laboratories or both. This was not always so. In the early days of petroleum refining, batch stills (sometimes fired by lump coal or wood) were used to separate the crude petroleum into various boiling-range fractions. Such batch stills were also used to improve the quality of the rough fractions to make them suitable products for the market requirements of that era. The first acknowledged continuous refineries did not appear until the very early part of the twentieth century.

The typical refinery in the period from 1860 to 1900 was dedicated to the production of kerosine as its major product, a product used both for illumination and for space heating. Gasoline and the light naphthas had little use prior to the advent of the automobile in the 1890s and the heavy black oils found little industrial use before construction of the big central powerhouses for the generation of electricity, which commenced with the Pearl Street Station in New York City in 1882.

FIRE HAZARDS AND CORRECTIVE MEASURES

During the "Age of Kerosine," there were two major factors that resulted in the sale of kerosines having a tendency to ignite outside the lamps or appliances for which they were purchased. First, there was the limited technology available for quality control of the kerosine product. Second, there were a few unprincipled refiners and marketers who purposely adulterated the kerosine by adding gasoline or light naphthas for which there was little demand at that time.

Naturally, a number of fires resulted. Also, quite naturally, efforts were initiated to find methods to identify such adulterated kerosines and to control the transportation, handling, and use of kerosine and of other flammable liquids. Thus, two lines of remediation developed in parallel. One took the form of legal restrictions, while the other endeavored to improve the technology for refining petroleum and especially for providing a measure of the flammability hazard of a liquid.

Wray has examined the history of flash point standards and of the regulations and specifications using flash point temperatures to control hazards [5]. In 1862, only three years after Drake's discovery well was completed in Pennsylvania, the United Kingdom enacted the Petroleum Act that defined a liquid having a flash point temperature below 100°F (37.7°C) as flammable. Seven years later, in the United States, the city of New Orleans passed an ordinance that defined a flammable liquid as one having a flash point temperature below 110°F (43.3°C) and required its labeling as such. At the U.S. federal level, Congress enacted a law in 1871 covering the safe handling of hazardous materials aboard ships and assigned its administration to the Coast Guard. Most of the nations of the world had laws regarding hazardous liquids by 1890.

The need for flash point measurements resulted in the evolution of a number of different designs of apparatus. A number of these are listed in Appendix A. Brief biographies of four individuals who did much to establish the foundation of flash point technology and whose names are associated with apparatus still used today are provided in Appendix B. These men were: Sir Frederick Abel in the United Kingdom; Adolf Martens and Berthold Pensky in Germany; and Charles J. Tagliabue in the United States.

The Abel closed-cup tester was established in 1879 by the British Parliament as the test apparatus that had to be used to meet the requirements of the 1862 Petroleum Act [5]. The flash point temperature for flammable liquids was simultaneously lowered to 73°F (22.7°C). The Abel apparatus (described in International Organization for Standardization [ISO] Standard ISO13736 Petroleum Products–Determination of Flash Point–Abel Closed Cup Method) is still in use. In fact, it is one of two referee methods used internationally for releasing aviation turbine fuels.

Early in the twentieth century in the United States, the ASTM (now called ASTM International) standardized a number of the flash point methods that had evolved [5]. Committee D02 on Petroleum Products and Lubricants, standardized the Tag closed-cup method as ASTM STM for Flash Point by Tag Closed Tester and issued the standard as ASTM Test Method D56-18T in 1918. This was followed by the ASTM Test Methods for Flash and Fire Points by Cleveland Open Cup (D92) and the test method for Flash Point by Pensky-Martens Closed Cup Tester (ASTM Test Method D93) in 1921. ASTM Committee D01 on Paint and Related Coatings, Materials, and Applications added the test method for Flash Point and Fire Point by Tag Open-Cup Apparatus (ASTM Test Method D1310) in 1952 and the test method for Flash Point of Liquids by Setaflash Closed-Cup Apparatus (ASTM Test Method D3278) in 1973. Committee D02 issued its own Setaflash test method, for Flash Point by Small-Scale Closed Tester (ASTM Test Method D3828) in 1979 and the test method for Flash Point by Continuously Closed Cup (CCCFP) Tester (ASTM Test Method D6450) in October 1999. This last-mentioned method uses a test specimen of 1 mL and detects the occurrence of a flash by an increase in pressure of 20 kPa or greater within 100 ms after the application of an arc ignition source. In 2004, ASTM Test Method D7094 for flash point by Modified Continuously Closed Cup Flash Point (MCCCFP) tester was adopted. A more recent flash point test method is the ASTM Test Method D7236 for Flash Point by Small Scale Close-Cup Tester (Ramp Method). It seems the evolution of flash point determinations continues

The above is not a full listing of ASTM or other flash point or flash/no-flash standards (see Appendixes C and D), nor does it include the long list of apparatus designs that have been proposed over the years (see Appendix A). These flash point methods merely illustrate the evolution that has occurred.

A number of international and national standards bodies, and numerous trade associations and other groups, have contributed to the development of flash point standards or have used flash point tests in other specifications or standards. The ISO operates through national standards bodies organized into a number of technical committees to develop its standards [6]. Probably the two ISO technical committees that have contributed most to ISO flash point standards are those dealing with petroleum products and lubricants and with paints and varnishes. The European community of nations has accepted many ISO standards as the standards to be used by its various member standards bodies.

In the United States, the American National Standards Institute (ANSI) is the official representative in ISO and, among other things, coordinates the voluntary development of national standards [7]. ANSI lists ASTM Test Methods D56 (Tag Closed Tester), D92 (Cleveland Open Cup), D93 (Pensky-Martens Closed Cup), and D3828 (Setaflash Closed Tester) as such American standards.

In other countries, we have acronyms such as SAA (Standards Association of Australia), BSI (British Standards Institution), SCC (Standards Council of Canada), AFNOR (Association Francais de Normalisation), DIN (Deutsches Institut für Normung), and JISC (Japanese Industrial Standards Committee) [6].

Many nations have trade groups, professional societies, and other organizations that have flash point standards or that use flash point tests in specifications or other standards. As examples, in the United States, such diverse groups as the American Oil Chemists Society, the American Association of State Highway Transportation Officials (AASHTO), the Chemical Specialties Manufacturers Association, the Factory Mutual system, the National Fire Prevention Association (NFPA), and Underwriters Laboratories (UL) all have interests in flash point measurements [7].

SCOPE OF BOOK

The contents of this book are intended for those who run flash point tests or for the user of the results of such tests. The significance and current-day use of flash point have been briefly noted above and are examined in greater detail in Chapter 2. Then, after defining the terminology used in flash point and associated technology in Chapter 3, the text compares a few representative types of flash point apparatus (manual, automated, and online) in Chapter 4. Sampling, sample handling, and the acquisition of test specimens is covered in Chapter 5. The preparation, maintenance, and checking of apparatus are discussed in Chapter 6. This is followed by a comparison of the procedures used with the various typical apparatus and materials tested, in Chapter 7, including the correction of results when the atmospheric pressure is other than 101.3 kPa and the reporting of results. The precision (repeatability and reproducibility) and the bias of the various methods are discussed in Chapter 8, which also explores the sources of experimental variation. Finally, various proposed methods of calculating the flash point and the limitations of such calculations are examined in Chapter 9. The calculation methods include, for example, the calculation of the flash point of blends when the flash points or other related properties of the components are known. The body of the manual is followed by a series of appendices containing supplementary material.

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2

The Significance and Current Use of Flash Point Test Methods

INTRODUCTION AND SCOPE

In the previous chapter, we explained why and how flash point testers and test methods came into being. However, that development occurred over a hundred years ago, so the question naturally arises whether flash point is still a significant and useful property of liquids in the current era of sophisticated instrumentation. The answer is a resounding, "yes!" Flash point remains a major means of categorizing the relative hazards associated with the shipping and handling of flammable liquids and is used in countless government and industrial regulations for that purpose.

This chapter first examines the general significance and use of flash point as stated in various standard test methods for flash point. It continues with examples of specific applications noted by Wray in his 1992 manual [1–8]. It ends with examinations of the use of flash point in the petroleum industry through the specifications of ASTM Committee D02 on Petroleum Products and Lubricants, and in the paint and coating industry through the specifications of the ASTM Committee D01 on Paint and Related Coatings, Materials, and Applications.

THE SIGNIFICANCE AND USE OF FLASH POINT

A section on significance and use is mandatory in all ASTM test method standards. ASTM Test Method D56 (Tag closed-cup tester) states that flash point measures the tendency of the specimen to form a flammable mixture with air under controlled laboratory conditions [9]. However, D56 cautions that flash point is only one of a number of properties that must be considered in assessing the overall flammability hazard of a material. Furthermore, D56 notes that 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 can indicate gasoline contamination. Most ASTM standard test methods for flash point have similar statements.

ASTM Test Method D56 also states that flash point is used in shipping and safety regulations to define flammable and combustible materials, but it cautions us to consult the specific regulations involved for precise definitions of those classes. ASTM Test Method D93 (Pensky-Martens Tester) states that the U.S. Department of Transportation (DOT) and the U.S. Department of Labor's Occupational Safety and Health Administration (OSHA) have established that liquids with a flash point under 100°F are flammable for those liquids that have a kinematic viscosity of 5.8 mm^2/s (cSt) or more at 37.8°C [10]. The regulations of these departments should be consulted for exact details. In ASTM Test Method D3143, we find that the test method is useful in determining that an asphalt cutback has been prepared with solvents that meet the desired range of flammability, and that the product has not been contaminated with lower flash point solvents [11].

USES OF FLASH POINT

General

In his 1992 *Manual on Flash Point Standards and Their Use,* Wray has provided a long list of uses of flash point in specifications, government regulations, and many codes and regulations of municipal groups both in the United States and in other nations. The following are some highlights.

Uses in ASTM Specifications

Flash points appear in numerous ASTM specifications as a parameter that must be met [1]. In 1992, the 36 ASTM specifications cited included four fuel specifications (for fuel oils, aviation turbine fuels, nonaviation turbine fuels, and kerosine); specifications for raw tung oil, raw linseed oil; and three solvents (mineral spirits, high-flash aromatic naphthas, and VM&P [varnish maker and painter] naphthas) used in the paint industry; and specifications for such products as dry-cleaning solvents, asphalts used for various purposes, chlorinated aromatic hydrocarbons used for capacitors and transformers, mineral insulating oil for electrical apparatus, electrical insulating varnishes, solvent floor polishes, lotion soap, and lubricating oils.

Uses in U.S. Government Specifications

There are a number of U.S. federal and military specifications that have flash point as a required parameter [2]. The Navy's Specification MIL-F-359 for the old black oil known as Navy Special Fuel Oil (a cut-back residual fuel used for shipboard boilers) had a requirement for a minimum flash point of 66°C by ASTM Test Method D93 or a minimum flash point of 93°C using ASTM Test Method D92 (Cleveland open-cup tester) [12]. The Navy's current multipurpose Naval Distillate F76 Fuel covered by Specification MIL-F-16884 has a requirement for a minimum ASTM Test Method D93 flash point of 60°C.

The U.S. Air Force has specifications for several aviation turbine fuels. The better known fuels are covered by Specifications MIL-T-5624 and MIL-T-83133 Aviation Turbine Fuel, which are usually referred to as JP-5 and JP-8 fuels, respectively. The former has a requirement of 60°C minimum, and the latter has a requirement of 38°C minimum, both measured by ASTM Test Method D93.

Both the Air Force and the Navy have specifications for missile fuels (MIL-P-87107 and MIL-P-82522, respectively) that have flash point requirements. Both of those fuels must meet ASTM Test Methods D93 or alternatively D3828 (Small Scale closed tester) flash point minima ranging from

16° to 52°C for the several grades of Air Force missile fuel and from 140° to 175°F for the Navy missile fuel [13].

U.S. Standards Organizations; Combustible and Flammable Liquids

Eleven standards organizations in the United States were cited as having flash point standards or standards using flash point [3]. Among others, the American National Standards Institute (ANSI), the American Association of State Highway Transportation Officials (AASHTO), the International Conference of Building Officials (ICBO), the National Fire Prevention Association (NFPA), and the Underwriters Laboratories (UL) were mentioned. NFPA and UL have, for example, developed flash point based classifications as a means of indicating the relative hazard of liquids [3].

NFPA defines a combustible liquid as one having a flash point at or above 37.8°C (100°F) and a flammable liquid as one having a flash point below that level and having a vapor pressure not exceeding 40 psia at 37.8°C. Furthermore, NFPA places liquids in one of three classes and a number of subclasses. Class I liquids are those having flash points below 37.8°C (100°F) with three subclasses. Class IA consists of those liquids with a flash point below 22.8°C (73°F) and with a boiling point below 37.8°C (100°F). Class IB liquids are those with the same flash point required by Class IA but with a boiling point at or above 37.8°C (100°F). Class IC liquids are those with a flash point at or above 22.8°C (73°F) but below 37.8° (100°F). Class II liquids are those having flash points at or above 37.8°C (100°F) but below 60°C (140°F), and Class III are those having flash points above that level. Class III liquids are divided into two subclasses, with Class IIIA consisting of liquids with flash points below 93.4°C (200°F) and Class IIIB consisting of liquids with flash points at or above 93.4°C (200°F). Flash points are determined by ASTM Test Methods D56, D93, D3278 [14] (Setaflash closed-cup tester), or D3828, depending upon the viscosity of the liquid, the level of the flash point, and whether the liquid contains suspended solids or tends to form a surface film.

The UL is well known to the general public through the prominent UL insignia on electrical cords and appliances. However, its laboratories also conduct evaluations to establish the relative flammability of liquids. The liquid is then placed in a given class and given a numerical rating. For example, a paraffin oil with a flash point of 440°F is given a rating of 100.

U.S. Code and Tariff-Writing Organizations

Three organizations in this category are: the Association of American Railroads Hazardous Materials Systems; the United Parcel Service (UPS); and the Building Officials and Code Administrators International (BOCA) [4]. As an example of what such organizations do, BOCA has established three classes of flammable liquids based upon their flash points. Their classifications are, to all intents and purposes, the same as those of the National Fire Prevention Association given above. However, they cite only ASTM Test Methods D56 and D93. Further, BOCA defines another category of liquid in addition to combustible liquids and flammable liquids. A volatile flammable material is any liquid, gas substance, mixture, or compound that readily emits flammable vapors at a temperature below 73°F (23°C) when tested in accordance with ASTM Test Method D56.

Local Government Regulations in the United States

Eight sets of state and municipal regulations serve as examples of regulations defining hazardous materials such as flammable or combustible materials that invoke the use of flash point measurements [5]. These are regulations of the states of Michigan, New Jersey, Ohio, and Pennsylvania; the cities of Baltimore, New York, and Philadelphia; and Baltimore County in Maryland.

In Pennsylvania, for example, there are three pertinent sections of their state laws: Titles 34, 37, and 67. Title 34 provides building classifications based on the nature of solvents used in the building. Thus, Class I buildings are those in which flammable petroleum solvents having closed-cup flash points lower than 100°F (37.8°C) are used. Class II buildings are those using solvents with flash points between 37.8°C and 59°C, with other solvent limitations such as initial boiling point; and Class III buildings are those using solvents using flammable petroleum solvents with closed-cup flash points not lower than 59°C.

Pennsylvania Title 37 covers state police regulations. These define a combustible liquid as one having a flash point at or above 100°F and below 200°F, and a flammable liquid as one having a flash point below 100°F and a vapor pressure not exceeding 40 psia at 100°F. The Tag closed-cup tester, the Cleveland open-cup tester, and the Pensky-Martens closed-cup tester are specified for determining the flash point; the choice depends upon the liquid's properties. Pennsylvania Title 67 covers hazardous materials in transportation and defines combustible liquids, flammable liquids, and other hazardous materials according to 49 CFR, the Code of Federal Regulations.

New York City's Administrative Code 27 is applied by the fire department when a permit is requested to transport, sell, or store chemical specialty products in the city. This code defines flammable liquids, combustible liquids, diesel fuel oil, and kerosine on the basis of ASTM Test Method D1310 (Tag open-cup tester) [15]. Flammable liquids are defined as those with flash points below 100°F, and combustible liquids are those with flash points from 100–300°F (37–148°C). Diesel fuel oil is any liquid used as a motor fuel that does not have a flash point below 100°F, and kerosine is any liquid product of petroleum that is commonly used for illuminating purposes and that does not have a flash point below 100°F. The New York City regulations for the storage and use of chemicals (in college, university, hospital, research, and commercial laboratories) have similar definitions for flammable and combustible liquids but specifies ASTM Test Method D56.

In summary, a number of states and local government agencies use flash point to define and regulate the transportation, use, and storage of hazardous materials within their respective jurisdictions.

U.S. Government Regulatory Agencies—Government Regulations

One of the most important uses of flash point has always been in government rules, regulations, and laws [6]. At the federal level, a number of regulations of the DOT, the Department of Labor's OSHA, and other such groups have been compiled and published as the CFR. The following are examples of CFRs in which flash point is used. Wray's manual or the original CFR should be consulted for details.

Sixteen CFR covers rules and regulations of the Consumer Product Safety Commission (CPSC). Subchapter C, which presents regulations issued pursuant to the Federal Hazardous Substances Act, defines an "extremely flammable" substance as one having a flash point at or below −6.7°C (20°F), a "flammable" substance as one with a flash point above that level but below 37.8°C (100°F), and a "combustible" substance as one having a flash point above 37.8°C (100°F). It specifies that flash points shall be based on ASTM Test Method D1310.

Twenty-nine CFR covers OSHA regulations for industrial plants (Part B) and for the construction industry (Subchapter D). One section of Part B contains a number of definitions relating to flammable and combustible liquids. This section defines the conditions under which ASTM Test Methods D56 and D93 are to be used. (Through a Program Directive, OSHA also recognizes the use of the Setaflash tester and ASTM Test Method D3278 for testing flammable and combustible liquids.) The division between flammable and combustible liquids is again 37.8°C (100°F). Organic peroxides, which undergo auto-accelerating thermal decomposition, are excluded from any of the specified flash point methods. A Hazardous Communication Section requires the communication of hazards associated with chemicals to workers and users of such materials and specifies protective laboratory practices and equipment for laboratory workers. Shipyard, marine terminals, and painting operations are also covered in detail.

Subchapter D covering the construction industry uses a different division between combustible and flammable liquids. It defines a combustible liquids as one having a flash point at or above 60°C (140°F) but below 93.4°C (200°F), and a flammable liquid as one having a flash point below 60°C (140°F) and a vapor pressure not exceeding 40 psia at 37.8°C (100° F).

Thirty-three CFR covers Coast Guard regulations for shipping on the St. Lawrence Seaway. These regulations state that a vessel shall be deemed a hazardous cargo vessel under a number of specified conditions. Two of these mention flash point. The first specifies a tanker as a hazardous cargo vessel if it is carrying fuel oil, gasoline, crude oil, or other flammable liquids in bulk, having a flash point below 61°C (141.8°F), including a tanker that is not gas free where its previous cargo had been such a cargo. The second specifies a tanker carrying certain specified materials in IMO Class 3, i.e., in excess of 50 tons of flammable liquids having a flash point below 61°C (141.80°F).

Forty CFR covers regulations of the U.S. Environmental Protection Agency (Part D). For pesticides and toxic substances, these regulations specify certain warnings regarding their flammability or explosive characteristics, depending in part on their flash points. ASTM Test Methods D93 and D3278 are specified. The regulations further specify that ignitable wastes shall not be disposed of in chemical waste landfills and defines liquid ignitable wastes as having a flash point less than 60°C (140°F) by ASTM Test Methods D93 or D3278.

Forty-six CFR covers regulations of the U.S. Coast Guard governing marine bulk shipments, commercial fishing vessels used in petroleum product transport, hazardous ship stores, and related matters. For bulk shipments, flammable liquids are defined as those having open-cup flash points at or below 26.7°C (80°F), and combustible liquids are those with flash points higher than that level. Three subclasses of flammable liquids (Grades A, B, and C) and two subclasses of combustible liquids are recognized defined by their vapor pressure for flammable liquids and by their flash point for combustible liquids. Flash point is defined as being determined by an open-cup tester, with other flash point values specified for ASTM Test Methods D56 Tag closed tester or for D93 Pensky-Martens closed tester. Similar definitions apply to vessels used to transport petroleum products in the fishing industry.

Forty-nine CFR Part A covers regulations of the U.S. Department of Transportation, Research, and Special Programs Administration (RSPA). Subchapter C, which lists hazardous materials regulations, covers a large number of classes. Class 3 includes flammable liquids and combustible liquids. Flammable liquids are defined as those with a flash point of not more than 60.5°C (141°F) unless the liquid qualifies under definitions in a group of materials such as aerosols and cryogenic liquids. A combustible liquid is defined as one having a flash point higher than the maximum noted above and less than 93°C (200°F) and does not meet the definition of any other hazard class. ASTM Test Methods D56, D93, and D3278 are specified depending upon the flash point. The regulations also assign packaging groups depending upon the flash point. (CAUTION: There are infinite details in the regulations. The excerpts given here pertain only to the use of flash point in classifying the hazardous materials.)

One thing is obvious from these excerpts from the various CFRs. Each must be used in context and studied in detail because the definitions for terms such as flammable liquids and combustible liquids are not consistent from one CFR to the next or even within a single CFR if dealing with different areas or categories of substance.

Specifications of Other National Governments

In 1992, nine countries were cited as having their own national standard specifications [7]. One of the nine nations, the Union of Soviet Socialist Republics (USSR), has dissolved into a number of independent units. Table 2.1 lists the countries and the required minimum flash point requirement in degrees Celsius for the various grades of aviation fuels, together with the specified flash point method.

In addition to such government specifications, there are several other specifications that are widely used. The IATA (International Air Transport Association) specification for kerosine-type aviation fuel calls for a minimum ASTM Test Methods D56 or D3828 of 38°C. The Detroit Diesel Allison specification for kerosine-type (diesel) fuel requires a minimum flash point of 105–150°F also by ASTM Test Methods D56 or D3828. Finally, the General Electric specification for kerosine-type turbine fuel requires a minimum ASTM Test Methods D56 or D3828 flash point of 100°F.

FLASH POINT METHODS IN COMMITTEE D02 SPECIFICATIONS

Overview

The *2011 Annual Book of Standards* (vol. 05.01 through 05.04) contains 36 standard product specifications over which Committee D02 on Petroleum Products and Lubricants has jurisdiction. Twenty-two are specifications for fuels for various purposes; eight are specifications for lubricating oils, industrial lubricants, or hydraulic fluids; and six are specifications for a miscellany of materials. The alphanumeric designations

TABLE 2.1—Specified Minimum Flash Points of Kerosine-Type Aviation Fuels According to the National Specifications of Various Countries

Country	Fuel Grade or Type	Min.F.Pt.(°C)	Test Method
Australia	Jet A-1	38	D3828
	AVTUR	38	D3828
Brazil	OAV-1	40	D56
Canada	Kerosine	38	D56/D3828
	High Flash Kerosine	60	D93
France	AIR 3405 D	41	D93
	AIR 3405 C	60	D93
Japan	Class 1 (Jet A-1)	38	D56
	Class 2 (Jet A)	38	D56
Peoples Republic of China	RP-3	38	N.S.[a]
	RP-1	28	261
	RP-2	28	261
Sweden	FLYGFOTOGEN 75	38	IP 170
United Kingdom	AVTUR	38	D56/D3828
			IP 170
	AVCAT	60	D93/IP34
U.S.S.R.	T-1	30	GOST 6356-75
	TS-1 Regular	28	GOST 6356-75
	TS-1 Premium	28	GOST 6356-75
	RT	28	GOST 6356-75

[a] Not shown.

and product names are listed in Tables 2.2, 2.3, and 2.4, respectively. Not all of these specifications include flash point as a requirement. Furthermore, not all are discussed, but are given for completeness and to bring the information up to date. For those not discussed, refer to the relevant ASTM standard specifications.

Fuel Specifications

Table 2.5 summarizes the flash point requirements placed upon the various types and grades of fuel in Committee D02 specifications. Some of these specifications have flash point requirements. The others are either LPG, aviation gasoline, or automotive spark ignition fuels. None of these has flash point requirements because such fuels are all very volatile and hence would have very low flash points. In fact, the automotive spark ignition fuels (gasoline, in common parlance) were, for many years, combined with air in carburetors before being introduced into an engine's cylinder and hence needed to be sufficiently volatile. Furthermore, the volatility of finished gasoline as measured by its vapor pressure is adjusted for the season of the year to preclude vapor lock in the summer and to insure sufficient volatility in the winter.

Two specifications require some but not all grades to meet flash point requirements. Thus, ASTM Specification D1655 for aviation turbine fuels covers two grades of fuels described as relative high flash point distillates of the kerosine type (Jet A and Jet A-1) and one grade (Jet B) described as relatively wide range volatile distillate [16]. As shown in Table 2.5, the kerosine type Jet A and Jet A-1 have flash point requirements, whereas the Jet B fuel does not.

Similarly, ASTM Specification D2880 for nonaviation gas turbine fuel oils includes a Grade 0-GT that has no minimum flash point requirement [17]. This Grade 0-GT is described as including naphtha, Jet B, and other light hydrocarbon liquids that characteristically have low flash point and low viscosity as compared with kerosine and fuel oils. The specification states that, when the flash point is below 38°C or when the kinematic viscosity is below 1.3 mm^2/s or when both conditions exist, the turbine manufacturer should be consulted with respect to safe handling and fuel system design.

In all cases where a flash point requirement has been imposed, the specified test method is ASTM Test Method D93 "except where other methods are prescribed by law." In all fuels except marine fuels, ASTM Test Method D3828 is permitted as an alternate, with ASTM Test method D93 as the referee method. ASTM Specification D2069 for marine fuels permitted ISO Test Method 2719 (the ISO Pensky-Martens method) as an alternative to ASTM Test Method D93

TABLE 2.2—Specifications for Fuels
ASTM D396 Standard Specification for Fuel Oils
ASTM D910 Standard Specification for Aviation Gasoline
ASTM D975 Standard Specification for Diesel Fuel Oils
ASTM D1655 Standard Specification for Aviation Turbine Fuels
ASTM D1835 Standard Specification for Liquefied Petroleum (LP) Gases
ASTM D2069[a] Standard Specification for Marine Fuels
ASTM D2880 Standard Specification for Gas Turbine Fuel Oils
ASTM D3699 Standard Specification for Kerosine
ASTM D4814 Standard Specification for Automotive Spark-Ignition Engine Fuel
ASTM D5797 Standard Specification for Fuel Methanol (M&)-M85) for Automotive Spark-Ignition Engines
ASTM D5798 Standard Specification Fuel Ethanol (ED75–ED85) for Automotive Spark-Ignition Engines
ASTM D6227 Standard Specification for Grade 82 Unleaded Aviation Gasoline
ASTM D6448 Standard Specification for Industrial Burner Fuel from Used Lubricating Oils
ASTM D6615 Standard Specification for Jet B Wide-Cut Aviation Turbine Fuel
ASTM D6751 Standard Specification for Biodiesel Fuel (B100) Blend Stock for Distillate Fuels
ASTM D6823 Standard Specification for Commercial Boiler Fuels with Used Lubricating Oils
ASTM D7223 Standard Specification for Aviation Certification Fuel
ASTM D7467 Standard Specification for Diesel Fuel Oil, Biodiesel Blends (B6-B20)
ASTM D7544 Standard Specification for Pyrolysis Liquid Biodiesel
ASTM D7547 Standard Specification for Unleaded Aviation Gasoline
ASTM 7592 Standard Specification for Grade 94 Unleaded Aviation Gasoline Certification Test Fuel
ASTM 7719 Standard Specification for High-Octane Unleaded Test Fuel

[a] The Marine Fuel specification is being dropped from the *Annual Book of Standards*. An International Organization for Standardization (ISO) standard contains the same information.

TABLE 2.3—Specifications for Lubricating Oils, Industrial Lubricants, and Hydraulic Fluids
ASTM D4293 Standard Specification for Phosphate Ester–Based Fluids for Turbine Lubrication
ASTM D4304 Standard Specification for Mineral Lubricating Oil Used in Steam or Gas Turbines
ASTM D4485 Standard Specification for Performance of Engine Oils
ASTM D4682 Standard Specification for Miscibility with Gasoline and Fluidity of Two-Stroke-Cycle Gasoline Engine Lubricants
ASTM D4859 Standard Specification for Lubricants for Two-Stroke-Cycle Spark-Ignition Gasoline—TC
ASTM D5760 Standard Specification for Performance of Manual Transmission Gear Lubricants
ASTM D6158 Standard Specification for Mineral Hydraulic Oils
ASTM D7044 Standard Specification for Biodegradable Fire Resistant Hydraulic Fuels

[18,19]. Many of the specifications that required flash points of 38°C or higher for the lighter grades, permit the use of ASTM Test method D56 (the Tag Closed Cup) for those grades provided the flash point is below 93°C, and the viscosity is below 5.5 mm^2/s at 40°C. However, if ASTM Test Method D56 is used, the specifications caution that the test method will give slightly lower values than ASTM Test Method D93. ASTM Test Method D93 remains the referee method.

A specification frequently has a section indicating the significance of the property specified. In these fuel specifications, the significance of the flash point requirements usually refers to its relationship to fire hazard and to the fact that flash point is usually regulated by law. For example, ASTM Specification D396 for fuel oils states, "The flash point of a fuel oil is an indication of the maximum temperature at which it can be stored and handled without serious fire

TABLE 2.4—Specifications for Miscellaneous Products
ASTM D4171 Standard Specification for Fuel System Icing Inhibitors
ASTM D4806 Standard Specification for Denatured Fuel Ethanol for Blending with Gasolines for Use as Automotive Spark-Ignition Engine Fuel
ASTM D4950 Standard Specification and Classification of Automotive Service Greases
ASTM D5983 Standard Specification for Methyl Tertiary-Butyl Ether (MTBE) for Downstream Blending with Automotive Spark-Ignition Fuel
ASTM D7450 Standard Specification for Performance of Rear Axle Gear Lubricants Intended for API Category GL-5 Service
ASTM D7618 Standard Specification for Ethyl Tertiary-Butyl Ether (ETBE) for Blending with Aviation Spark-Ignition Fuels

TABLE 2.5—Flash Point Specified in Fuel Specifications

Spec. No.	Type of Fuel	Grade	Min. Fl.Pt.,°C	STM	Alt. STM
D396	Fuel Oil	1, 2	38	D93	D56[a]; D3828
		4L	38	D93	D3828
		4, 5L, 5H	55	D93	D3828
		6	60	D93	D3828
D975	Diesel Fuel	1-D, 1-D LS	38	D93	D56[a]; D3828
		2-D, 2-D LS	52	D93	D56[a]; D3828
		4-D	55	D93	D3822-D
D2069[b]	Marine Fuels	DMX	43	D93	ISO 2719
		DMA, DMB, DMC	60	D93	ISO 2719
		15 Grades Resid.	60	D93	ISO 2719
D2880	Gas Turbine	1-GT, 2-GT	38	D93	D56[a]; D3828
		3-GT	55	D93	D3828
		4-GT	66	D93	D3828
D3699	Kerosine	1-K, 2-K	38	D56	D3828
D6448	Industrial Burner	RFO4	38	D93	D56[a]; D3828
	Fuel from Used Lubes	RFO5L, RFO5H	55	D93	D3828
		RFO6	60	D3828	
D6751	Biodiesel	B100	130	D93-C D3828, D6450	
D6823	Com. Boiler Fuel	RFC 4	38	D93-B D3828, D56, D6450	
	From Used Lubes	RFC 5L	55	D93-B D3828, D6450	
		RFC 5H	55	D93-B D3828, D6450	
		RFC 6	60	D93-B D3828, D6450	
D7223	Turbine Fuel		Report	D93	D3828
D7544	Pyrolysis Biofuel			45	D93-B
D7467	Biodiesel	B6-B20, S15	52[c]	D93-C	D56[a]; D3828
		B6-B20, S500	52[c]	D93-C	D56[a]; D3828
		B6-B20, S5000	52[c]	D93-C	D56[a]; D3828

Note: For other fuel specifications not covered, flash point is not a specification requirement. See relevant ASTM specification for details.

[a] ASTM Test Method D56 is allowed as an alternate flash point test method provided the flash point is < 95° C and the kinematic viscosity is < 5.5 mm^2/s.

[b] The marine fuel specification is being dropped from ASTM standards as it duplicates an ISO standard.

[c] When a cloud point of < −12 °C is specified, minimum flash point is 38° C

hazard [20]. The minimum permissible flash point is usually regulated by federal, state, or municipal laws and is based on accepted practice in handling and use." ASTM Specification D975 for diesel fuels adds the information that flash point is not directly related to engine performance but is "important in connection with legal requirements, and is normally specified to meet insurance and fire regulations" [21]. ASTM Specification D6751 is unique in stating, "The flash point for biodiesel is used as the mechanism to limit the level of unreacted alcohol in the finished fuel" [22].

Specifications for Lubricating Oils, Industrial Lubricants, and Hydraulic Oils

Table 2.6 summarizes the flash point requirements for the various types of lubricating oils and hydraulic oils in Committee D02 specifications. There are no flash point requirements in ASTM Specifications: D4682, Specification D4859, or Specification D5760 [23–25]. Also, there is no flash point requirement in ASTM Specification D4485 for type SJ engine oils other than those falling in SAE Grades 0W-20, 5W-20, 5W-30, and 10W-30.

In the four specifications where there is a flash point requirement, that requirement is specified solely by ASTM Test Method D92, except in ASTM Specification D4485, where ASTM Test Method D93 is given as an alternate with flash points 15°C below their Cleveland open-cup values.

Various significances are given for the flash point requirements in these specifications. Several specifications state that flash point is used primarily for quality control. ASTM Specification D4485 states that flash point provides a means for determining whether any residual solvents or other low boiling fractions remain in the finished oil [26]. ASTM Specification D6158 for hydraulic oils states that flash point is "mainly of interest as a quality control test and for regulatory reasons. However, some manufacturers use it as a safety criterion for work at high temperatures" [27].

Miscellaneous Specifications

Only one of the six miscellaneous Committee D02 specifications has a flash point requirement, and that is Specification D4171 for Fuel System Icing Inhibitors [28]. However, the requirement applies only to Type III fuel system icing inhibitors, i.e., diethylene glycol monomethyl ether, which is used in both aviation gasoline and in aviation turbine fuel. The requirement is a minimum flash point of 85°C measured by ASTM Test Methods D93, D56, or D3828. There is no specific significance given for the need for this requirement.

TABLE 2.6—Flash Point Specifications for Lubricating Oils, Industrial Lubricants, and Hydraulic Oils

Specification Number	Type of Material	Viscosity Grade	D92 COC °C, Min	
			Flash	Fire
D4293	Phosphate Ester Fluids	ISO 32	225	325
		ISO 46	225	325
D4304	Turbine Lubricating Oil-Type I	ISO 32/46/68/100	180	-
	- Type II	ISO 68/100	180	-
		ISO 150	210	-
D4485	Engine Oils—Type SH	SAE 5W-30	200	
		SAE 10W-30	205	
		SAE 5W-40	215	
	Type SJ	SAE 0W-20	200	
		SAE 5W-20	200	
		SAE 5W-30	200	
		SAE 10W-30’	200	
D6158	Mineral Hydraulic Oils	ISO 10		125
		ISO 15		145
		ISO 22		165
		ISO 32		175
		ISO 46		185
		ISO 68		195
		ISO 100		205
		ISO 150		215

FLASH POINT IN THE PAINTS AND COATINGS INDUSTRY[1]

Normal Combustible Hazard Control

As in the petroleum industry, flash point is important in the paints and coatings industry, especially for the shipping, handling, and transport of these materials. For the common solvents, both hydrocarbon and nonhydrocarbon types used in the industry, ASTM Test method D56 is primarily used to determine flash point. ASTM Test Methods D1310 and D3941 (Equilibrium Test Method) can be used as well [29]. Although ASTM Test Method D93 is applicable to paint materials, it is seldom used because of the difficulty in cleaning the instrument after a flash point determination of such material.

For the finished paint products, there is a flash point test method specifically under the jurisdiction of ASTM Committee D01 on Paints and Coatings, i.e., ASTM Test Method D3278. This test method uses only 2 mL of sample and is very similar to ISO3679 (Rapid Equilibrium Method) and ISO 3680 (Flash/No Flash Rapid Equilibrium Method) [30,31].

Special Tests

Mixtures of flammable liquids and nonflammable liquids (such as alcohol and water mixtures in water-based paints) are classified by the U.S. government as a flammable liquid on the basis of a closed-cup flash point method. Thus, mixtures may be classified as flammable even though they do not sustain burning. ASTM D4206, which is also under ASTM Committee D0l's jurisdiction, determines the ability of a liquid to sustain burning [32]. When used with a closed-cup flash point method, the test method provides a measure of the flammability of the mixture. ASTM Test Method D4206 is similar to ISO 9038, "Determination of the Ability of Liquid Paints to Sustain Combustion" [33].

Typical and Specification Flash Points

Typical D56 flash point values of solvents used in the paint and coatings industry may be found in Table 2.7. Such typical flash points are normally greater than the minimum flash points shown in comparable specifications. As examples of

TABLE 2.7—Flash Point of Materials Used in the Paints and Coating Industry (All by Test Method D56)

MATERIAL	ASTM SPECS	FLASH PT. (°C)	FLASH PT (°F)
Hydrocarbon Solvents			
Hexanes	D1836	< –18	< 0
Heptanes		–8	18
Lacquer Diluent		–7	20
VM&P Naphtha Type I	D3735	5	41
VM&P Naphtha Type II	D3735	27	81
VM&P Naphtha Type III	D3735	5	41
Mineral Spirits Type I	D235	42	108
Mineral Spirits Type II	D235	61	142
Mineral Spirits Type III	D235	40	104
Mineral Spirits Type IV	D235	40	104
Deodorized Kerosine		61	142
Mixed Xylenes	D84	28	83
Ortho-Xylene	D5471	32	90
Meta-Xylene		27	81
Para-Xylene	D5136	27	81
Ethyl Benzene		21	70
High-Flash Aromatics Type I	D3734	42	108
High-Flash Aromatics Type II	D3734	66	150
Cyclohexane		–20	–4
Terpene Solvents			
Wood Turpentine	D13	35	95
Dipentene		49	120
Pine Oil		54	130

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[1] Courtesy of R. G. Montemayor

TABLE 2.7—Flash Point of Materials Used in the Paints and Coating Industry (All by Test Method D56) (Continued)

MATERIAL	ASTM SPECS	FLASH PT. (°C)	FLASH PT (°F)
Ketone Solvents			
Acetone	D329	–18	0
Methyl Ethyl Ketone (MEK)	D740	–7	20
Methyl Isobutyl Ketone (MIBK)	D1153	16	60
Methyl Isoamyl Ketone (MIAK)	D2917	36	96
Methyl *n*-Amyl Ketone (MAK)	D4360	39	102
Diacetone Alcohol	D2627	49	120
Isophorone	D2916	82	180
Ester Solvents			
Methyl Acetate		–18	0
Ethyl Acetate	D4614	–4	24
Isopropyl Acetate	D3131	2	35
n-Propyl Acetate	D3130	13	55
Isobutyl Acetate	D1718	17	65
n-Butyl Acetate	D4615	27	81
n-Amy1 Acetate	D3540	38	101
Methyl Amy1 Acetate	D2634	36	96
n-Hexyl Acetate	D5137	57	134
n-Butyl Propionate		38	100
n-Pentyl Propionate		57	135
2-Ethoxyethyl Acetate	D3728	52	126
PM Acetate	D4835	46	114
Glycol Ether Solvents			
2-Methoxy Ethanol	D3128	39	103
2- Ethoxy Ethanol	D331	42	108
2-Butoxy Ethanol	D330	66	150
PM Glycol Ether	D4837	34	94
DPM Glycol Ether	D4836	75	167
Alcohol Solvents			
Methanol	D1152	11	52
Ethanol (Anhydrous)		13	55
Isopropanol	D770	12	54
n-Propanol	D3622	23	74
sec-Butanol	D1007	29	85
Isobutanol	D1719	23	74
n-Butanol	D304	36	97
n-Amy1 Alcohol	D319	33	91
Methyl Isobutyl Carbinol	D2635	39	103
2-Ethyl Hexanol		73	164

this, let's look at ASTM Specifications D235 for Mineral Spirits, D3734 for High-Flash Aromatic Naphthas, and D3735 for VM&P Naphthas [34–36].

ASTM Specification D235 sets a minimum of 38°C for Type I, Type III, and Type IV Mineral Spirits and a minimum of 61°C for Type II High Flash Point Mineral Spirits. The typical values shown in Table 2.7 are 42°, 40°, and 40°C for Types I, III, and IV and are 61°C for Type II Mineral Spirits. ASTM Specification D3734 has a minimum flash point of 38°C for Type I Aromatic Naphthas and 61°C for Type II, whereas the typical values are 42°C and 66°C, respectively.

Finally, ASTM Specification D3735 has set a minimum flash point of 4°C for Types I and III VM&P Naphthas and 23°C for Type II, whereas the typical values run 5°C for both Types I and III, and 27°C for Type II.

CHAPTER SUMMARY

- Flash point measures the tendency of a material to form a flammable mixture with air under controlled laboratory conditions. Flash point can also indicate the presence of highly volatile and flammable materials in a relatively nonvolatile or nonflammable material.
- Flash point is used in specifications as a parameter to be met. Flash point is also used to classify liquids as flammable or combustible. Flash point is used in countless national and local regulations regarding the transportation, storage, and use of flammable and combustible materials.
- ASTM Committee D02 on Petroleum Products and Lubricants has jurisdiction over 36 product specifications used in the petroleum industry. Of these, 11 of 22 fuel specifications, 4 of 8 specifications for lubricating oils and hydraulic fluids, and 1 of 6 miscellaneous specifications use flash point as one of the parameters that must be met.
- Flash point is important in the paint and coatings industry, especially in the transportation and storage of its raw materials and finished products. ASTM Committee D01 on Paints and Related Coatings, Materials, and Applications has standardized numerous test methods for determining flash points and burning points of materials under its jurisdiction.
- Because the various flash point tests give somewhat different results, it is important to use those test methods, and only those tests, cited in a specification or regulation.

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3

Explanation and Definition of Terms

INTRODUCTION

Flash point provides a means of determining the relative combustibility of liquids. Hence, we will first discuss some aspects of combustion before examining terms related to flash point, flash point apparatus, and flash point test methods. The chapter will end with a description and discussion of two phenomena that affect the determination of flash point, specifically, a phenomenon in which a film is formed on the surface of the flash point sample and one in which the sample contains nonflammable components that interfere with the determination of flash point.

COMBUSTION

In school, most of us have been exposed to information on the causes and nature of fires and flames. We learned about the fire triangle, i.e., the need for a fuel, air, and an ignition source before a fire can start. We learned too about the parts of a candle flame or Bunsen burner flame, and we were told that all flames result from combustion in the gaseous phase. We may also have heard that there are limits to the relative amounts of air and fuel that will support a flame. If there is too little fuel in the gaseous mixture, there will be no flame; the mixture is too "lean." If there is too little air (oxygen) present, there will also be no flame; the mixture is too "rich." Let us look at these phenomena in more detail.

In the normal combustion reaction, molecules of oxygen in the air component react with molecules of the combustible component in an exothermic (heat-generating) process. When a combustion mixture is too lean, the fuel molecules are too far apart to be energized by the heat released at the ignition source. In short, the reaction cannot be propagated. The reverse is true when a mixture is too rich. In the latter case, the oxygen molecules are too far from the site of the initial reaction to receive enough of the liberated heat energy to propagate the reaction. This is, of course, a greatly simplified explanation of a very complex thermodynamic process.

The concentration of fuel molecules when the mixture has just reached the point at which combustion can be propagated is termed the "lower flammable limit," and the condition when the amount of oxygen is just too little relative to the fuel molecules, to propagate combustion is called the "upper flammable limit." The two terms have been defined in several ASTM Standard Test Methods, specifically, in ASTM Test Method E681 and in ASTM Practice E918 as follows:

lower limit of flammability or **lower flammable limit (LFL)** *n.*–The minimum concentration of a combustible substance that is capable of propagating a flame through a homogeneous mixture of the combustible and a gaseous oxidizer under the specified conditions of test.

upper limit of flammability or **upper flammable limit (UFL)** *n.*–The maximum concentration of a combustible substance that is capable of propagating a flame through a homogeneous mixture of the combustible and a gaseous oxidizer under the specified conditions of test [1,2].

ASTM Test Method E681 notes that the LFL and UFL of gases and vapors define the range of flammable concentrations in air. Therefore, these concentrations can be used to determine guidelines for the safe handling of volatile chemicals, e.g., in assessing ventilation requirements for the handling of gases and vapors. For hydrocarbons, the break point between nonflammability and flammability is not sharp at the lower flammability limit but, rather, occurs over a narrow concentration range. The break point is even less distinct at the upper limit. Practice E918 points out that limits of flammability obtained in relatively clean vessels must be interpreted with care. Under industrial conditions, surface effects due to carbon or other deposits can significantly affect the limits of flammability.

STOICHIOMETRIC CONSIDERATIONS

Upon combustion, a hydrocarbon fuel is converted into carbon dioxide (CO_2) and water (H_2O) if there is sufficient oxygen present for complete reaction. When compounds containing the heteroatom nitrogen are present, oxides of nitrogen are also formed, and the mixed nitrogen oxides are usually referred to as NO_x. Similarly, when compounds of the heteroatom sulfur are present, oxides of sulfur are formed, and these are referred to as SO_x.

When a hydrocarbon is converted to CO_2 and H_2O, it requires more than one molecule of oxygen (O_2) to complete the conversion. This becomes obvious in the following equation (3.1), in which we use octane as the typical hydrocarbon.

$$2\ C_8H_{18} + 25\ O_2 \rightarrow 16\ CO_2 + 18\ H_2O \qquad (3.1)$$

Even more molecules of O_2 are required when larger hydrocarbon molecules are involved. If there is a lack of O_2 molecules, at least some carbon monoxide (CO) will probably be formed.

COMBUSTION WITHOUT AN IGNITION SOURCE

Although an ignition source is normally needed to initiate combustion, this is not always the case. Autoignition, spontaneous combustion, and compression ignition result without the agency of an ignition source. In autoignition, the heat liberated by the oxidation of the fuel component of a gaseous mixture containing an oxidizer cannot escape entirely through the wall of the confining vessel, thus resulting in a rapid increase in temperature. Consequently, this results in an equally rapid increase in the reaction rate so that an explosion can occur. ASTM Test Method E659 for Autoignition Temperature of Liquid Chemicals defines this phenomenon as:

autoignition, *n.*–the ignition of a material, commonly in air as the result of heat liberation due to an exothermic oxidation reaction in the absence of an external ignition source such as a spark or flame [3].

This phenomenon will not occur until the rate of heat generated by the exothermic reaction is greater than the heat being dissipated through the walls of the containing vessel. Hence, there is a system temperature below which this will not occur, an autoignition temperature defined in ASTM Test Method E659 as:

autoignition temperature, *n.*–The minimum temperature at which autoignition occurs under the specific conditions of test.

ASTM Test Method E659 further states that this temperature is also referred to as the spontaneous ignition temperature, the self-ignition temperature (SIT), and the autogenous ignition temperature (AIT).

The second of the phenomena resulting in combustion without the use of an external ignition source is often called "spontaneous combustion." Spontaneous combustion results from a build up of heat developed in a system without means of dissipating the heat generated. For example, if some rags are soaked in a flammable liquid and thrown into a heap, the oxidation of the oil generates heat. Because the rags prevent free flow of air and dissipation of the heat, the system can become so hot that the rags burst into flame.

The third phenomenon in which an external source of ignition is not required is known as compression ignition. Compression ignition is the principle that underlies what most people call the diesel engine. (For this reason, engineers and scientists have begun to call it the compression-ignition engine to contrast it with the spark-ignition engine that most of us know as the gasoline or Otto engine.) In the diesel engine, air and fuel are compressed to a greater extent than in a gasoline engine. This compression results in both a heating of the fuel-air mixture and a closer proximity of the molecules of air to those of the fuel. Consequently, the oxidation of the fuel becomes very rapid, the volume of gases increases, and the piston in the engine's cylinder is pushed away from the cylinder head, thereby facilitating combustion In some respects, this may be considered a special case of autoignition.

FLASH POINT APPARATUS

As Appendix A shows, numerous types of flash point apparatus have been designed, built, and used over the years. They are all different, but they are all similar in their fundamental features. In all cases, a sample of combustible liquid is placed in a vessel in contact with air, the liquid is heated, and the temperature at which the application of an ignition source creates a flash across the surface of the liquid is taken as the flash point. In essence, each inventor was trying to simulate a real-life situation and, using his simulation, was comparing the tendency of different liquids to ignite if an ignition source was present.

Over the years, the technical community has settled upon and standardized relatively few designs of apparatus. These are usually designated either by the inventor's name or by some characteristic of design, and by whether the apparatus is an open-cup or a closed-cup design. An open-cup apparatus may be considered a simulation of a fluid spill in an open area subject to minor drafts of air. A closed-cup apparatus, on the other hand, may be considered a simulation of a spill of liquid in a confined area.

Apparatus may also be distinguished as manual or automatic (unattended operation). The older designs of flash point apparatus were originally designed for manual operation, i.e., the operator measured out the test specimen, regulated the heating of the sample to keep the rate of temperature increase at that specified by the test method, applied the ignition source at specified temperature intervals, and watched for the flash. In fact, in some of the earlier instruments, the ignition source was a flaming splinter that the operator introduced into the cup. However, to obtain control over the flame size, this technique was replaced with gas-fed flames of specified size. Several of the older types of apparatus have now been automated so that little is required beyond measuring out the test specimen. The apparatus is often unattended during the flash point determination phase. In fact, even that task of sample changing has been reduced. Apparatus has been designed for the automatic changing of sample cups so that, as one test is completed, the sample cup is moved away from the lid and a new one containing the next test specimen to be tested is automatically placed in position.

The older type of apparatus used substantial volumes of sample for the test specimen. For example, the Tag closed-cup tester (ASTM Test Method D56) requires a test specimen of 50-mL size [4]. However, the type of tester now called the small-scale tester in ASTM Test Method D3828 requires as little as 2 mL [5]. The most recently standardized test apparatus, the continuously closed-cup tester of ASTM Test Method D6450, uses even less sample, with its test specimen being only 1 mL in size [6].

FLASH POINT PROCEDURES

Just as there are different types of flash point apparatus, there are different types of test procedures. Procedures are designed to either determine the flash point temperature or to determine whether a flash point has been reached at a specified temperature (the so-called flash/no-flash tests). Flash point tests in turn may be divided into dynamic or equilibrium flash point tests. The following definitions are based on definitions for the adjectives "dynamic" and "equilibrium" in ASTM Test Method D93 (the Pensky-Martens closed-cup method) [7].

dynamic flash point, *n.*–A flash point determined by a procedure where the vapor above the test specimen and the test specimen are not in temperature equilibrium at the time the ignition source is applied.

equilibrium flash point, *n.*–a flash point determined by a procedure where the vapor above the test specimen and the test specimen are at the same temperature at the time the ignition source is applied.

Some procedures yield dynamic and others yield equilibrium flash points because the designs of apparatus are different. There may even be two or three different procedures within a single test method. For example, in ASTM Test Method D93, which uses the same apparatus in three different ways, there are three procedures (Procedures A, B, and C) to accommodate differences in the materials tested [7]. Procedure A is used for distillate fuels and for other homogeneous petroleum liquids. Procedure B is used for residual fuel oils, cutback residua, used lubricating oils, mixtures of petroleum liquids with solids, petroleum liquids that tend to form a surface film under the conditions of the test, and petroleum liquids of such viscosity that they would not be uniformly heated under the heating and stirring conditions of Procedure A. Procedure C is applicable to biodiesel materials. Procedure A uses a heating rate of 5–6°C per minute, and the stirrer that is part of the Pensky-Martens design is rotated at 90–100 rpm. In contrast, Procedure B for the heavier, more viscous materials uses a slower heating rate (1–1.5°C) and a faster stirrer rotation (250 ± 10 rpm) while Procedure C has a heating rate of 3°C per min and a stirring rate of 90–120 rpm. All three procedures are dynamic procedures.

In any flash point test, there are a number of rate processes. The transfer of heat through the walls of the test cup is time dependent. Once through the walls of the test cup, the heat transfer to the liquid adjacent to the wall of the cup is another rate process. The band of heated liquid is less dense than the remaining liquid in the test cup and hence will rise though the heavier unheated liquid. This produces a natural circulation, conveying heat to other parts of the test cup. This too is a rate process. The stirrer, if part of the apparatus and if used in the test procedure, imposes a mechanical circulation of liquid. This increases the heat transfer rate and eliminates pockets of cold liquid. However, the vapor in the space above the liquid must be heated by the liquid with which it is in contact, and, if the heating rate of the liquid is too fast, the vapor temperature will lag the liquid temperature, thus resulting in a dynamic rather than an equilibrium flash point procedure. Finally, vapor molecules must diffuse to the level where the ignition source is applied, and this too is a rate process. In short, the sequence of rate processes tends to produce a dynamic process rather than a system equilibrium.

Equilibrium flash point procedures tend to use a slower heating rate than the dynamic procedures. However, true equilibrium conditions may not be reached in practice because the temperature may not be uniform throughout the test specimen, and the test cup cover and shutter on the apparatus may be cooler than the test specimen. Regardless of minor discrepancies, such slow temperature rise procedures are considered equilibrium procedures.

One other variable in flash point measurement that must be considered is the barometric pressure. If two laboratories, one at sea level and one, say, in the mile-high city of Denver, were to run flash point tests by the same flash point procedure and faithfully followed all the directions of that procedure, they would still come up with different observed flash point temperatures. Therefore, flash point methods include a correction of all flash points to what they would be at sea level under a standard barometric pressure of 101.3 kPa. We can now define "flash point" or, more exactly, "flash point temperature." The following definition is that found in ASTM Test Method D93 [7].

Flash point, *n.*–In petroleum products, the lowest temperature corrected to a barometric pressure of 101.3 kPa (760 mm Hg), at which application of an ignition source causes the vapors of a specimen of the sample to ignite under specified conditions of test.

This same definition has been used in the rest of the flash point methods under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants. The test specimen is deemed to have "flashed" when a flame appears and instantaneously propagates over the entire surface of the test specimen. When the ignition source is a test flame, the application of the test flame may cause a blue halo or an enlarged flame prior to the actual flash point, but these phenomena are not "flashes" and should be ignored.

SPECIAL FLASH POINT SITUATIONS

The operator of flash point apparatus should be aware of two special phenomena. The first is the tendency of some materials to form surface films during the course of the flash point test; the second is called "flash point masking." (Flash point masking was originally termed "outgassing.")

The first of these is described in ASTM Test Method D92, the flash point procedure using the Cleveland open-cup tester, an apparatus that does not normally include a stirring mechanism (some automatic units are equipped with a stirring paddle for minimizing surface film formation) [8]. A note in the procedure regarding determinations of the flash point of asphalt (a substance that tends to form a surface film) advises the operator to carefully move the surface film to the side of the test cup, e.g., by using a spatula, before each application of the ignition source. The note explains that, otherwise, higher flash point temperatures will be recorded. The implication is that the surface film inhibits the movement of molecules into the vapor space, thus creating a delay before a flash point concentration of molecules is obtained. An alternative technique using a filter paper to inhibit the formation of the surface film is also appended. Regardless of the technique used, the operator should be aware of the phenomenon and take precautions or suffer the chance of getting an erroneously high flash point result.

The flash point masking phenomenon can occur when a liquid mixture contains a nonflammable component along with flammable components. Appendix X1 of ASTM Test Method D93 (the Pensky-Martens test method) explains that a nonflammable component tends to inert the vapor space above the liquid, thus preventing the observation of a flash when the ignition source is applied [7]. The flash point is masked so that an erroneously high flash point is reported or else a report of "no flash point" is made. This masking phenomenon most frequently occurs when ignitable liquids contain certain halogenated hydrocarbons such as dichloromethane (methylene chloride) or trichloroethylene.

In running a flash point test with such materials, no distinct flash is observed. Rather, there is a significant enlargement of the test flame and a change in its color from blue to yellow-orange. Continued heating and testing for flash point above ambient temperature can result in significant burning of ignitable vapors outside the test cup, often immediately above the test flame, thus presenting a potential fire hazard. Appendix X2 of ASTM Test Method E502, "Selection and Use of ASTM Standards for the Determination of Flash Point of Chemicals by Closed Cup Methods," suggests that, to evaluate mixtures of flammable and nonflammable components properly, tests should be run on the original materials, and then samples should be allowed to partially evaporate under conditions approximating those to be encountered in actual usage [9]. Flash point tests should be run on the residues remaining after various degrees of evaporation, and both closed-cup and open-cup tests might be advisable.

In a presentation to the former ASTM S15 Coordinating Committee on Flash Point, P. M. Kennedy suggested a number of dangers associated with a phenomenon that he referred to as "outgassing" [10]. First of all, it results in the reporting of erroneously high flash point temperatures, thus yielding an inaccurate assessment of the flammability dangers associated with the liquids. Secondly, it can result in the mislabeling of ignitable liquids under the Hazardous Substances Act so that there is a practical, if not legal, noncompliance with government regulations. Thirdly, there is a failure to warn users and handlers of the liquids of the true flammability dangers involved, so that manufacturers, shippers, and consumers underestimate the dangers associated with the liquids. This induces a false sense of security that can lead to fires with resultant burn injuries or even deaths, plus property damage. Kennedy also proposed a definition for the phenomenon and suggested its inclusion in all appropriate flash point standards. The following definition is derived from the Kennedy proposal.

Flash point masking or **outgassing**, *n.*–A phenomenon in which a non-flammable material in a mixture with a flammable material or materials inerts the vapor space in a flash point test cup so that no flash point is obtained but, instead, the vapors ignite and form a flame above the ignition source when it is applied in the normal course of flash point testing.

Appendix X1 of ASTM Test Method E502 states that there are instances with pure materials where the lack of a flash point does not ensure freedom from flammability [9]. Some materials, such as trichloroethylene, require large diameters for flame propagation, and these materials will not propagate a flame in apparatus the size of a flash point tester. However, their vapors are flammable and will burn when ignited in apparatus of adequate size. The ASTM Test Method E502 Appendix further warns that some materials that produce very dense vapors that have a very narrow range of flammability or that need to be somewhat superheated to burn will not yield a flash point in the usual sense. However, they can form flammable vapor-air mixtures and they will burn if heating and mixing are optimal and if their temperatures are raised sufficiently.

CHAPTER SUMMARY

This chapter has examined combustion phenomena with and without an ignition source. It has discussed various types of flash point testers and various differences among flash point test procedures. Finally, it explains that there are special situations where flash point results can be affected by the properties of the liquid tested.

REFERENCES

[1] ASTM E681, “Standard Test Method for Concentration Limits of Flammability of Chemicals (Vapors and Gases),” *Annual Book of ASTM Standards*, ASTM International, West Conshohocken, PA.

[2] ASTM E918, “Standard Practice for Determining Limits of Flammability of Chemicals at Elevated Temperature and Pressure,” *Annual Book of ASTM Standards*, ASTM International, West Conshohocken, PA.

[3] ASTM E659, “Standard Test Method for Autoignition Temperature of Liquid Chemicals,” *Annual Book of ASTM Standards*, ASTM International, West Conshohocken, PA.

[4] ASTM D56, “Standard Test Method for Flash Point by Tag Closed Cup Tester,” *Annual Book of ASTM Standards*, ASTM International, West Conshohocken, PA.

[5] ASTM D3828, “Standard Test Method for Flash Point by Small Scale Closed Tester,” *Annual Book of ASTM Standards*, ASTM International, West Conshohocken, PA.

[6] ASTM D6450, “Standard Test Method for Flash Point by Continuously Closed Cup (CCCFP) Tester,” *Annual Book of ASTM Standards*, ASTM International, West Conshohocken, PA.

[7] ASTM D93, “Standard Test Method for Flash-Point by Pensky-Martens Closed Cup Tester,” *Annual Book of ASTM Standards*, ASTM International, West Conshohocken, PA.

[8] ASTM D92, “Standard Test Method for Flash and Fire Points by Cleveland Open Cup Tester,” *Annual Book of ASTM Standards*, ASTM International, West Conshohocken, PA.

[9] ASTM E502, “Standard Test Method for Selection and Use of ASTM Standards for the Determination of Flash Point of Chemicals by Closed Cup Methods,” *Annual Book of ASTM Standards*, ASTM International, West Conshohocken, PA.

[10] Kennedy, P. M. (John A. Kennedy and Associates, Inc.), “Outgassing Phenomenon in Flash Point Testing,” notes for presentation to ASTM S15 Coordinating Committee on Flash Point, 6 April 1994.

4

Flash Point Apparatus and Auxiliary Equipment

INTRODUCTION

Many different designs of flash point apparatus have been developed over the years (see Appendix A). However, only a few have stood the test of time and have been incorporated into flash point standards by such organizations as ASTM International; the Energy Institute (formerly known as the IP or Institute of Petroleum); and the International Organization for Standardization (ISO). In this chapter, we examine and compare the major features of two open-cup designs (the Tag and the Cleveland open-cup apparatus), three closed-cup designs (the Abel, the Tag, and the Pensky-Martens closed-cup apparatus), and automated versions of several of these. We shall also examine two newer designs, the small-scale (Setaflash), and the continuously closed-cup flash point (CCCFP) apparatus, both of which operate on somewhat different principles than the earlier designs. Finally, we shall take note of two items of ancillary equipment, the barometer and the sample changer.

Four of the manual types of apparatus bear the names of pioneers in the technology of flash point. The Abel closed-cup apparatus was invented by Sir Frederick Abel, and the Pensky-Martens closed-cup apparatus was developed by Adolf Martens and Berthold Pensky. The Tag open-cup and the Tag closed-cup testers carry a shortened form of the name of Charles Tagliabue. Brief biographies of these men may be found in Appendix B.

All of the early manual designs noted above may be considered essentially simulations of real-life situations: a spill of a material in a confined space in the case of closed-cup apparatus, and a spill in an open space in the case of an open-cup apparatus. In both cases, a sample is placed in a container (cup) and warmed. An ignition source is lowered at given temperature intervals to a specified depth in the vapor space above the liquid, and note is made of the liquid temperature at which ignition (a flash) occurs. These tests were usually dynamic tests, so the results are dependent upon the rate of heating and other factors in the design of the apparatus.

Below, we will compare the ways in which the various designs addressed the major elements of the flash point system. Primarily, this means the size of the sample, the size of the sample cup, and the distance from the surface of the liquid in the sample cup to the ignition source. Other dimensions can be found in the standards cited at the end of this chapter. The particular editions of those standards that were examined in the course of developing this chapter are also shown.

MANUAL OPEN-CUP APPARATUS

General Design Configurations

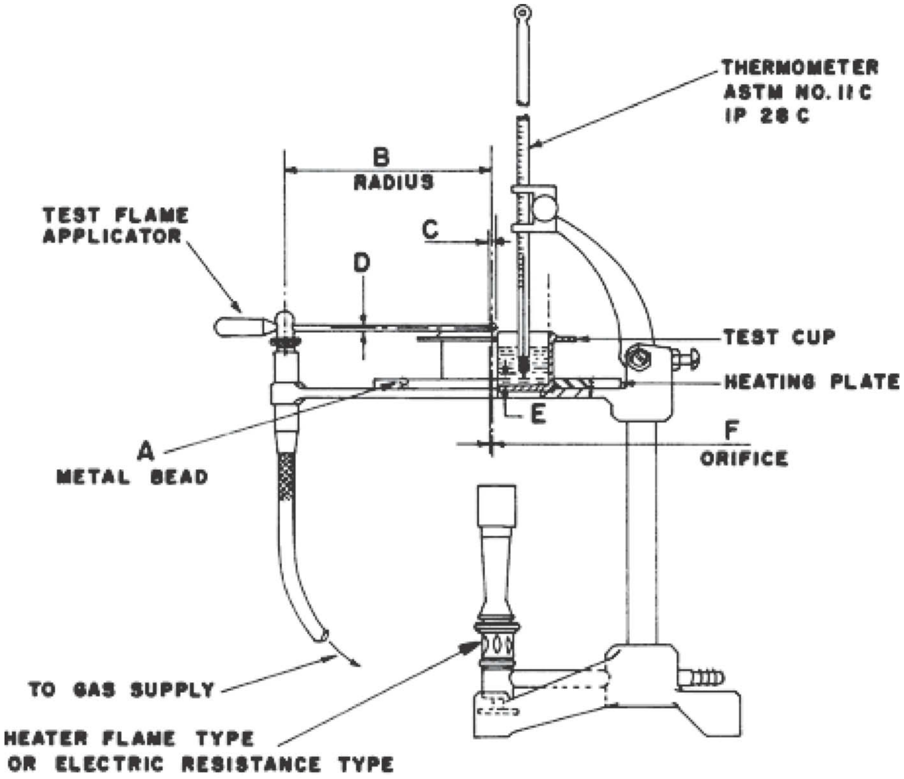
The two manual open-cup type of apparatus still in general use are the Cleveland described in Test Method D92 and the Tag described in ASTM Test Method Dl310 [1,2]. A schematic and a photograph of the Cleveland apparatus are shown in Figures 4.1 and 4.2, and a schematic and photograph of the Tag apparatus are shown in Figures 4.3 and 4.4. Note that the Cleveland uses either a gas flame or an electrical resistance heater to heat the sample and employs a metallic heating plate and a brass sample cup to provide dissemination of the heat to the sample in the cup. In contrast, the Tag apparatus uses a water or water-glycol bath at lower flash point temperatures or a silicone fluid bath at higher flash point temperatures to distribute the heat from a specified small gas burner or a permitted small electric heater. The Tag open-cup apparatus uses a glass sample cup surrounded by the liquid bath; the liquid bath container is made of copper, which also helps to distribute the heat.

Like all early manual flash point testers, both the Cleveland and the Tag instruments depend upon the human eye to detect the flash point. A test specimen is considered to have flashed when, upon application of the ignition source, a flame instantly propagates across the entire surface of the liquid. A blue halo or an enlarged test flame prior to the actual flash point should be ignored.

The Test Cup

The Cleveland test cup as specified in ASTM Test Method D92 is made of brass or other nonrusting metal of equivalent heat conductivity. It is essentially a right circular cylinder with a fillet of nominal 4-mm radius connecting the sides with the bottom plate. The sides of the cylinder are 2.25–2.5 mm thick, and the bottom plate is 2.8–3.5 mm thick. These thicknesses affect the conduction of heat so the tolerances are important. The internal diameter of the cylinder is 63–64 mm, and its internal height is 32.5–34 mm, with a filling mark inscribed 9–10 mm (0.354 to 0.394 inches) below the top of the cylinder, i.e., approximately 24 mm above the bottom plane. Consequently, the test cup is intended to hold a test specimen of about 75 mL.

The Tag test cup specified in ASTM Test Method D1310 is made of molded clear glass, annealed, heat resistant, and free from surface defects. It deviates from a right circular cylinder by having a slightly tapered side and a rounded bottom. Its maximum diameter is 2 in. (about 50.8 mm), and the maximum depth is 1 7/8 in. (about 47.6 mm). When filled with the test specimen, the liquid level is 1/8 in. (about 3.18 mm) below the top of the cup. Consequently, the cup holds a liquid test specimen of about 90 mL. (Note: The primary system of dimensions used in the methods is shown first. Furthermore, the estimated sizes of the test specimens in the Cleveland and Tag open-cup apparatus should not be used to measure out the test specimens. The Cleveland cup has a mark indicating the correct level of sample, and the



	millimetres		inches	
	min	max	min	max
A—Diameter	3.2	4.8	0.126	0.189
B—Radius	152	nominal	6	nominal
C—Diameter	1.6	nominal	0.063	nominal
D		2		0.078
E	6	7	0.236	0.276
F—Diameter	0.8	nominal	0.031	nominal

Figure 4.1—Schematic of a manual Cleveland open-cup flash point apparatus. (Courtesy of ASTM International D92.)

Figure 4.2—An example of a manual Cleveland open-cup flash point apparatus. (Courtesy of Koehler Instruments.)

Tag has a leveling device for the same purpose. Follow the instructions of the applicable ASTM Standard in filling the cups.)

The Ignition Source

For the Cleveland open cup, a natural gas (methane) or a bottled gas (butane, propane, or a mixture of the two) flame is suitable as the ignition source, with the tip of the flame having a suggested diameter of 3.2–4.8 mm. For the Tag apparatus, the ignition source is called an ignition taper, which is defined as a small, straight, blow-pipe type gas burner with the tip approximately 1/16 in. (about 1.5 mm) in diameter, i.e., approximately the same size as that of the Cleveland open-cup apparatus.

In the case of the Cleveland apparatus, the test flame is swept across the test cup on a radius not less than 150 mm (6 in.) with the center of the flame in a plane not greater than 2 mm (5/64 in.) above the rim of the cup. Hence, the flame will be 11–12 mm (about 0.43–0.47 in.) above the surface of the sample in the cup.

For the Tag apparatus, the ignition taper is maintained in a fixed horizontal plane above the test cup by means of a swivel device so that the test flame passes on the circumference of a circle having a radius of at least 6 in. (150 mm). The STM further specifies that the flame shall pass across the center of the cup in a plane 1/8 in. (3.2 mm) above the

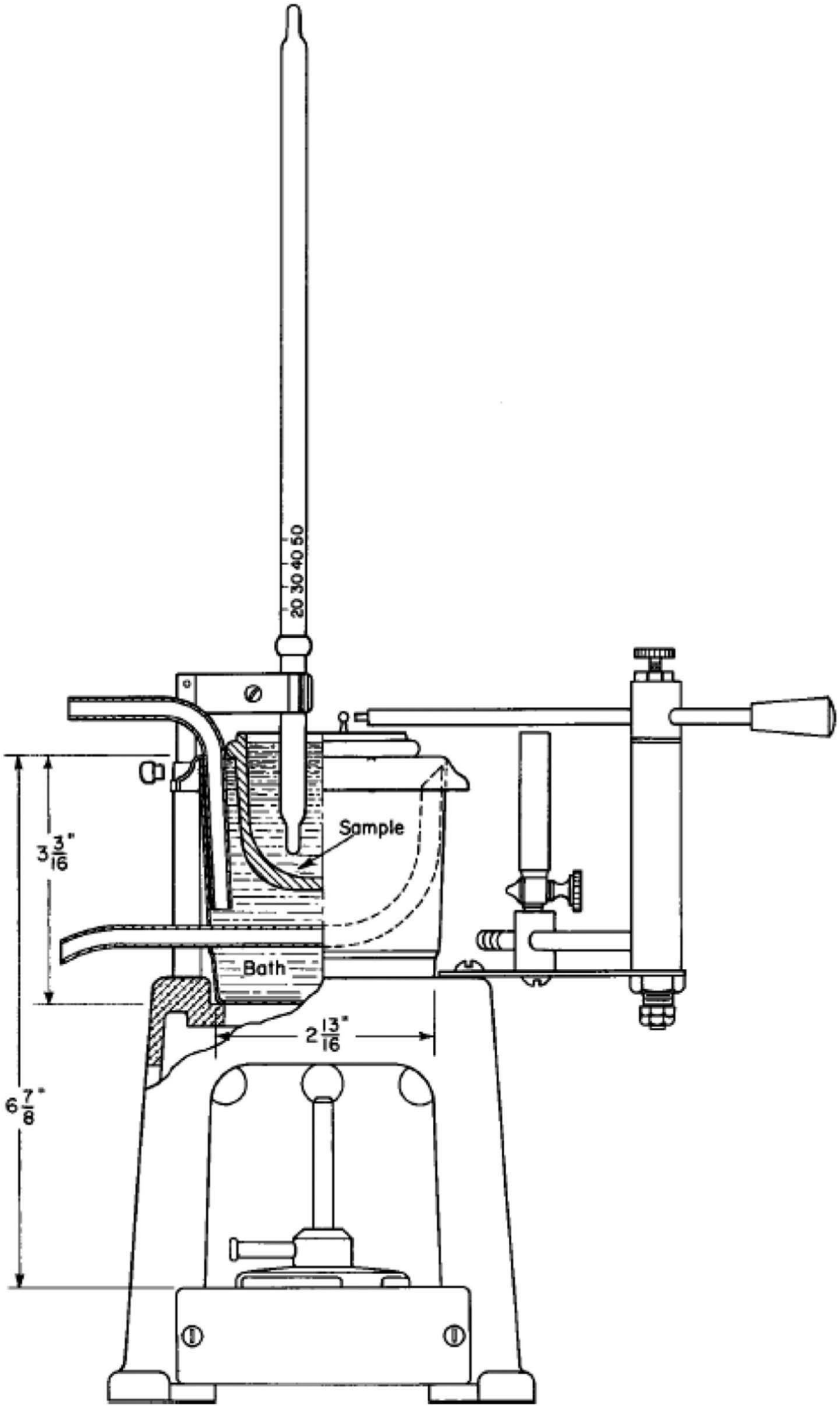


Figure 4.3—Schematic of a manual Tag open-cup flash point apparatus. (Courtesy of ASTM International D1310.).

upper edge of the cup as measured from the center of the orifice. Hence, the center of the Tag flame is to be 1/4 in. (6.35 mm) above the surface of the sample in the cup. Thus, the flame in the Tag apparatus is closer to the sample surface than that of the Cleveland apparatus, by about 0.18–0.22 in. (roughly 5 mm).

Temperature Measurement

Because flash point is the temperature at which a flash occurs when a source of ignition is applied, all flash point apparatus must incorporate a means of temperature measurement. In the older apparatus, this was a mercury-in-glass stem thermometer. In automated and other more modern

Figure 4.4—An example of a manual Tag open-cup flash point apparatus. (Courtesy of Koehler Instruments.)

apparatus, thermocouples and other means of temperature measurement may be applied.

It should be noted that Sweden has banned the use of mercury thermometers within its borders, and it has been predicted that other countries might soon follow Sweden's lead. It is, of course, the fear that toxic mercury could be released if a thermometer is broken that has led to this action. ASTM is working on the standardization of glass-stem thermometers containing no mercury but having the same response as mercury thermometers. However, it will be necessary to evaluate such nonmercury thermometers to determine whether they yield the same results in flash point apparatus as the original mercury-in-glass thermometers.

For the Cleveland apparatus, ASTM Test Method D92 specifies thermometers conforming to the requirements of ASTM Specification E-1 or those of IP Specification for the IP Standard Thermometers. For the range −6° to +400°C, ASTM thermometer 11C or IP thermometer 28C is used and, for the range 20–760°F, ASTM thermometer 11F is used. Alternatively, an electronic temperature-measuring device, such as a resistance thermometer or a thermocouple may be used if it exhibits the same temperature response as the mercury thermometers.

For the Tag open-cup apparatus, ASTM Test Method D1310 defines the thermometer as conforming to Specification E-1 and lists three thermometers for Fahrenheit measurements and three for Celsius measurements. The lowest Fahrenheit range covered is 0–60°F with thermometer 33F-75 being specified, and the highest is 299–325°F with thermometer 35F-79 being specified. The lowest Celsius range is −18° to +15°C where thermometer 33C-75 is used, and the highest is 93–165°C where thermometer 35C-79 is used. No alternative electronic measuring device is permitted.

MANUAL CLOSED-CUP APPARATUS

General Design Configurations

The three manual closed-cup designs still in general use are the Abel, the Tag closed cup, and the Pensky-Martens apparatus, described in Test Methods ISO 13736, ASTM Test Methods D56, and ASTM D93, respectively [3–5]. Schematics and photographs are shown in Figures 4.5 and 4.6 for the Abel apparatus, in Figures 4.7 and 4.8 for the Tag apparatus, and in Figures 4.9 and 4.10 for the Pensky-Martens apparatus.

All three of these closed-cup testers, like the two open-cup testers described above, use the human eye as the sensing device for the flash point, which can be observed while the shutter is open and the ignition source is being applied.

The Abel apparatus uses "any suitable device for heating the heating vessel, such as gas flame, electric heater or spirit lamp." The heating vessel is made of copper and consists of two flat-bottomed cylindrical vessels placed coaxially one inside the other. The space between the two vessels is used as a "water jacket" and is filled with an equivolume mixture of ethanediol and water (for the lower flash point measurements) or water (for the higher flash point measurements). The inner cylinder forms an air bath in which sits a brass test cup containing the test sample and fitted with a stirrer and thermometer. The test cup is fitted with a brass cover assembly containing a slide that can be moved to expose an opening through which a test gas jet flame can be directed.

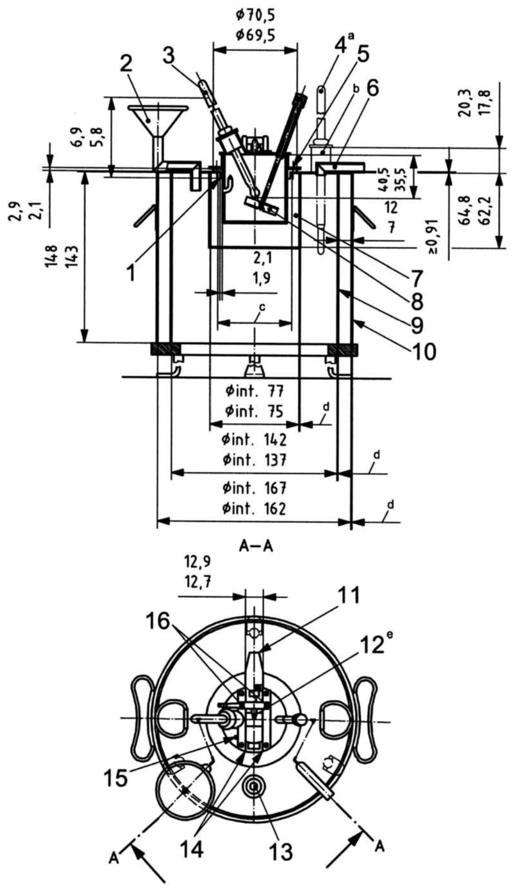
The Tag closed-cup tester uses a primary heater "of any type (electric, gas, alcohol, and so forth) capable of controlling temperature as required." However, an external electric heater controlled by a variable voltage transformer is recommended. The primary heater serves to heat a liquid bath containing a 1:1 mixture of ethylene glycol and water (for flash points below 13°C or above 60°C) or either water or a water-glycol mixture (for flash points between 13°C and 60°C). A 68-g test cup of brass or other nonrusting metal of equivalent heat conductivity is partially submerged in the bath liquid. A lid fitted with a shutter rests on the test cup. When activated, the shutter exposes an opening in the lid and directs an ignition source into the opening. In the Pensky-Martens apparatus, the primary heating source may be either a flame or an electric heater, so designed in either case that the temperature of the bottom and side walls are approximately the same. The primary heater supplies heat to a stove (an air bath, a metal casting, or an electric resistance element) and a top plate. The test cup is made of brass or other nonrusting metal of equivalent heat conductivity and is fitted with a brass cover. The cover is equipped with a brass shutter that can be activated to expose openings in the cover. When the shutter is in the open position, it depresses a test flame or an electric resistance-type igniter into the opening.

The Test Cups

The Abel test cup is a right circular cylinder with a uniform thickness of metal of 14 mm. It has an inside diameter of 49.5–52.0 mm and a depth of 55–57 mm. The depth of sample in the cup is controlled by a gauge so that it is 17.7–17.9 mm below the top of the cup. Hence, the sample size is approximately 78 mL.

The Tag closed-cup tester is essentially a right circular cylinder but has a rounded transition from the sides to the flat bottom. The metal cup has a uniform thickness of 0.90 ± 0.5 mm. The procedure calls for a sample of 50 ± 0.5 mL so the liquid surface is about 29.4 mm below the top of the cup.

The Pensky-Martens test cup is also essentially a right circular cylinder with an inside diameter of 50.72–50.85 mm and an inside depth of 55.75–56.00 mm. There is a filling mark 21.72–21.84 mm below the top of the cup, so the test



1 Ebonite or fiber ring, which fits easily on cup
2 Funnel
3 Test cup thermometer
4 Heating vessel thermometer
5 ø 2.2 × 3.8 for long CSK screws
6 Copper overflow pipe
7 Inner (air) chamber
8 Stirrer
  a For actual position, see plan view
  b Inside diameter of thermometer socket 15 mm to 15.5 mm
  c 2.5-mm maximum clearance in top plate
  d 0.6 mm copper
  e Length of jet is approximately 15 mm; the bore at the end to 15.5 mm of the jet is 1.71 mm maximum and 1.46 mm minimum

9 Heating vessel
10 Outer jacket
11 Slide 20 SWG 0.91 mm brass
12 Gas jet or pilot light
13 Heating vessel thermometer
14 Guides
15 White bead ø 3.6 mm to 4.1 mm of suitable material
16 Trunnions

Figure 4.5—Schematics for the Abel closed-cup flash point; dimensions in mm. (Courtesy of Energy Institute IP 170.)

sample is approximately 70 mL. The sides of the cup are 1.0 mm thick, and the bottom is 2.29–2.54 mm thick.

The Ignition Systems

The Abel ignition system uses a gas jet flame as its ignition source. When the cover slide is moved into the open position, the gas flame is tilted over the central hole into a position where "the lower edge of the cover bisects the circle formed by the bore of the jet when in the lowest position."

ASTM Test Method D56 for the Tag closed-cup apparatus states that natural gas and bottled gas flame igniters and electric igniters have been found acceptable for use as the ignition source. However, if a gas flame is used, the gas pressure must not exceed 3 kPa. The ignition source is constructed so that opening the shutter depresses the tip of the ignition source to a point approximately 2 mm to the right of the center of the middle opening of the lid, as this brings the ignition source to the approximate center of the opening. The plane of the underside of the lid is between the top and the bottom of the ignition source when the latter is fully depressed. These latter instructions obviously apply to a flame-type igniter.

ASTM Test Method D93 for the Pensky-Martens apparatus specifies that, when using a flame-ignition device, the tip shall have an opening of 0.69–0.79-mm diameter and shall preferably be made of stainless steel. When the shutter is moved into the open position, the tip of the flame-ignition device is simultaneously depressed so that the center of its orifice is between the planes of the under and upper surfaces of the cover and on a radius passing through the center of the larger opening. Simultaneously, the shutter opens other apertures that allow air to enter the vapor space. An

Figure 4.6—An example of a manual closed-cup Abel flash point tester. (Courtesy of Petrotest Instruments.)

electric igniter, which is also suitable, must be of the electric-resistance (hot wire) type and must position the heated section of the igniter in the aperture of the test cover in the same manner as the gas flame device.

Temperature Measurement

In the Abel apparatus, the temperature at which a flash occurs is measured with an "oil cup thermometer" that is specified in detail in ISO 13736. The required temperature range is −35° to +70°C, with subdivisions marked at 0.5°C intervals. It is stated that thermometer IP 74C conforms to these requirements. A thermometer socket mounted on the test cup cover assembly is designed to bring the bulb of the thermometer to a position vertically below the center of the cover and at the correct distance from it.

For the Tag closed-cup apparatus, ASTM Test Method D56 specifies the use of different ASTM thermometers as the test cup thermometer for different ranges of flash point. ASTM thermometer 57C (or 57F) is specified for flash points below 4°C (40°F). Thermometer 9C (or 9F), or alternatively 57C (or 57F) is specified for flash points at 4°C to 49°C (40–120°F), and thermometer 9C (or 9F) is specified for flash points above 49°C (120°F). However, it is stated that, when thermometers complying with ASTM requirements are not available, thermometers complying with the requirements for the EI (formerly the Institute of Petroleum, IP) such as thermometer IP 15C PM-Low can be used. The design of the test cup lid is such that the thermometer can be placed with the bottom of its bulb approximately in the horizontal center of the test cup and 45.0 ± 0.8 mm below the top of the cup.

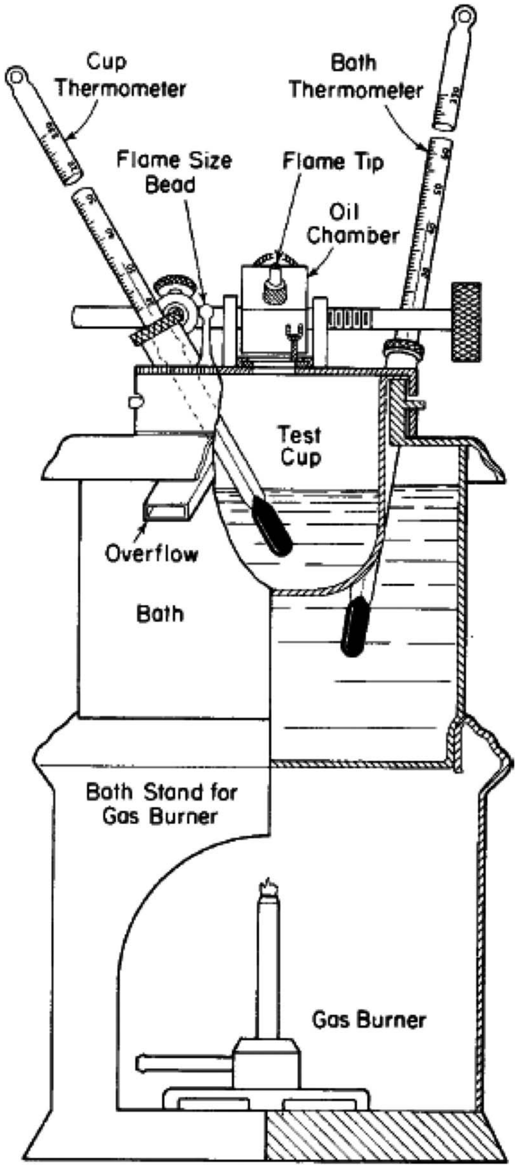


Figure 4.7—Schematic of a manual Tag closed-cup flash point apparatus. (Courtesy of ASTM International D56.)

For the Pensky-Martens apparatus, ASTM Test Method D93 specifies the test cup thermometers in great detail but, like the Tag closed-cup apparatus, specifies different thermometers for different flash point ranges. For flash points in the range of −5° to +110°C (20–230°F), the ASTM 9C (9F) thermometer is specified. For a flash point range of +10–200°C (50–392°F), an ASTM 88C (88F) thermometer is specified, and for a flash point range of +90–370°C (200–700°F), an ASTM 10C (10F) thermometer is specified. IP thermometers 15C, 101C, and 16C are shown as alternatives to the ASTM 9C, 88C, and 10C, respectively. Electronic measuring devices such as resistance thermometers or thermocouples are also permitted as long as they exhibit the same temperature responses as the mercury thermometers. A thermometer adapter built into the cover assembly insures that the bottom of the thermometer bulb is 43.0–46.0 mm below the top of the test cup.

Other Design Features

Both the Abel and the Pensky-Martens apparatus are fitted with stirrers that serve to eliminate hot spots in the liquid

Figure 4.8—An example of a manual Tag closed-cup flash point apparatus. (Courtesy of Koehler Instruments.)

sample as well as to enhance the transfer of heat from the heat source to the liquid. In the Abel apparatus, the stirrer is made of brass and consists of four blades mounted at a 45-degree angle to the shaft. From the tip of one blade to that of its opposite blade is roughly 28–29 mm. The shaft is at an angle to the vertical and rotation at 30 rpm is such that a downward thrust is created.

In the Pensky-Martens apparatus, the stirring device consists of a vertical shaft mounted in the center of the cover and carrying a pair of two-bladed metal propellers. The upper (smaller) one rotates in the vapor space; the lower (larger) one rotates in the liquid sample. The liquid propeller is approximately 38 mm from tip to tip with each of its 8-mm-wide blades pitched at about 45 degrees. When testing distillate fuels and other such lower viscosity materials (Procedure A), the stirring device is rotated at 90–120 rpm in a direction to generate a downward thrust. When testing residual fuels, heavier lubricating oils, and other such higher viscosity material (Procedure B), the stirring device is rotated at 250 ± 10 rpm, again in a direction to generate a downward thrust. For testing biodiesel material, Procedure C specifies a stirring rate of 90–120 rpm.

AUTOMATED APPARATUS

General Comments

Automated versions have been developed for many of the manual apparatus types described above and reference to these automated versions have been incorporated in the test methods. Thus, such references may be found in ASTM Test Method D92 for the Cleveland open-cup apparatus, in ISO 13736 for the Abel closed cup, in ASTM Test Method D56 for the Tag closed cup, and in ASTM Test method D93 for the Pensky-Martens closed-cup apparatus. Only ASTM Test Method D1310 for the Tag open cup lacks a mention of an automated version.

Descriptions of the automated versions are very limited. The usual specification is that automated versions use the same test cup (and, of course, the test cup cover for closed-cup apparatus) as that specified for the manual version and that the automated version be capable of following the test procedure specified for the manual apparatus. Photographs of automated versions of the Cleveland open-cup, the Abel closed-cup, the Tag closed-cup, and the Pensky-Martens closed-cup apparatus are shown in Figures 4.11 through 4.14.

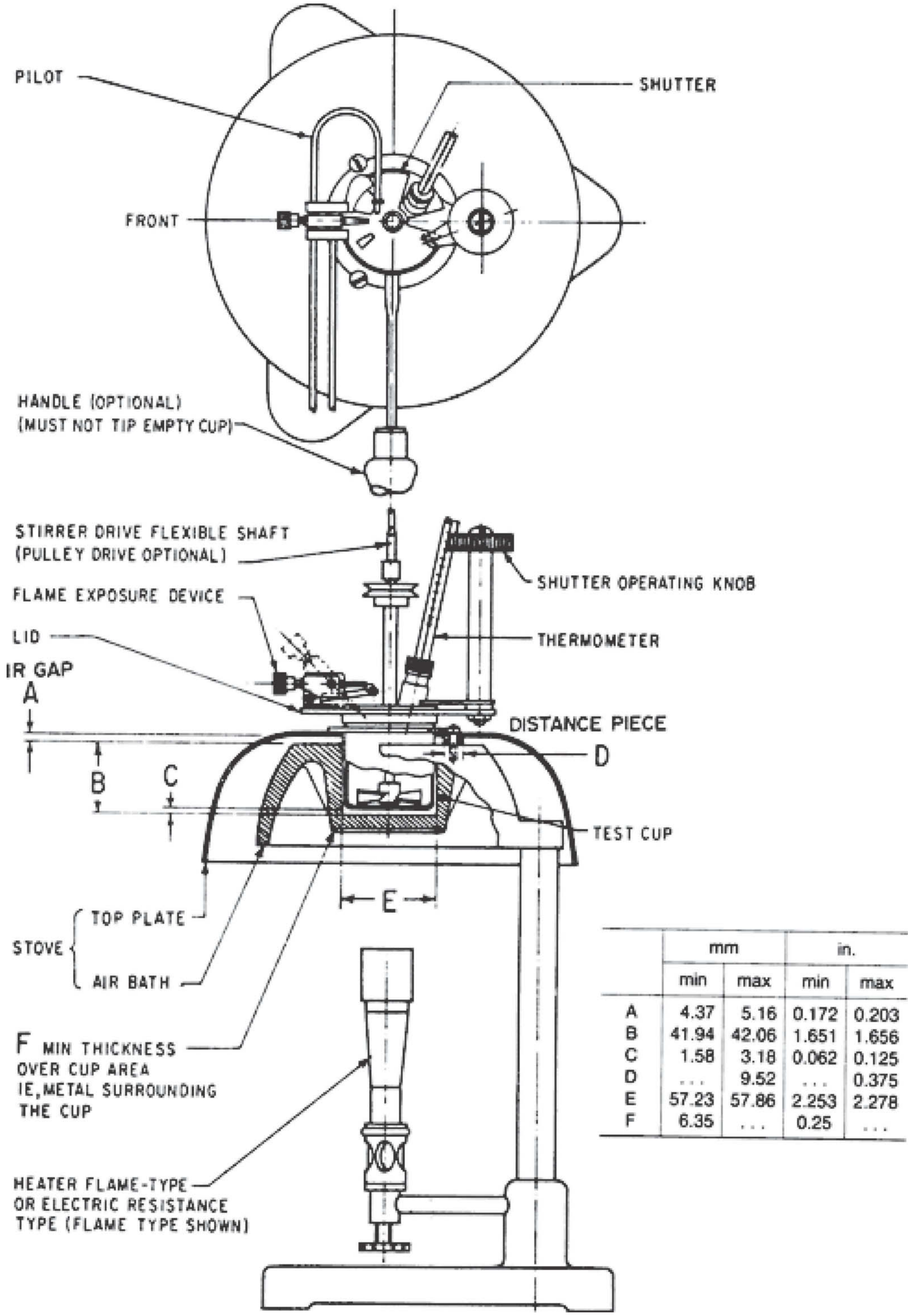
Because one advantage of automation is that it frees the operator to perform other chores, the automated versions of the manual methods use nonvisual method to detect the flash point. In general, the automated apparatus use either ionization detection or thermal detection. Ionization current detection employed in ASTM Test Method D92 uses a pair of electrodes placed immediately above the sample cup. These electrodes detect changes in ionization caused by the flash, which ionizes the vapor so that the voltage level across the ring electrodes drops momentarily. This drop, when it passes a given threshold level, is reported as the flash point. One problem with this system is the possibility of a false indication if the sample contains water, due to the conductivity of water vapor.

The thermal detection system, suitable for closed-cup methods such as ASTM Test Methods D56 and D93, senses a rapid increase in the vapor temperature that is caused by the flash. A low mass thermocouple is used, and the voltage increase generated by the increased temperature is reported as the flash point once it reaches a threshold value. The system is reliable and can be used when a sample contains water or alcohol contaminants like those potentially present in biodiesel fuel.

Requirements Specific to the Test Method

Because the way chosen by different manufacturers to control the procedure may vary, the user of such apparatus is instructed to follow the manufacturer's instructions in setting up, adjusting, and calibrating the apparatus. Below are summaries of instructions given in the various standard test methods.

ASTM Test Method D92 states that the automated Cleveland open-cup apparatus shall perform the test in accordance with the manual procedure, shall use the same test cup, and shall apply the test flame in the same manner as with the manual apparatus. ISO 13736 notes that Abel equipment that is partially or wholly automated may be used provided the results obtained with the automated apparatus do not differ from those obtained with the manual apparatus. Furthermore, the user of the automated apparatus is enjoined to follow the manufacturer's instructions for calibrating, adjusting, and operating the instrument. Results obtained manually are to be used as the referee method in any cases of dispute. ASTM Test Method D56 states that an automated Tag closed-cup tester may be used if it is capable of performing the test in accordance with the manual procedure. Such an automated apparatus may use either a gas test flame or an electric igniter, but the dimensions of the test cup, test cover, shutter, and gas ignition device (if gas ignition is chosen) must be the same as those of the manual apparatus. The user of the automated apparatus is instructed to follow all the manufacturer's instructions for calibrating, checking, and operating the equipment.



	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	. . .

Figure 4.9—Schematic of a manual Pensky-Martens closed-cup flash point apparatus. (Courtesy of ASTM International D93.)

ASTM Test Method D93 states that the automated Pensky-Martens closed-cup apparatus is an automated flash point instrument capable of performing the test in accordance with the Procedures A (less viscous material), B (more viscous material), and C (for biodiesel material) of the manual apparatus. Any automated apparatus must use the test cup, test cover and shutter, stirring device, heating source, and ignition source device specified for the manual apparatus. Both the manual and the automated versions are to be prepared for operation by following the manufacturer's instructions for calibrating, checking, and operating the equipment. For both Procedures A and B, the automated apparatus must control the heating rate, the stirring of the test specimen, the application of the ignition source, the

Figure 4.10—An example of a manual Pensky-Martens closed-cup flash point tester. (Courtesy of Koehler Instruments.)

Figure 4.11—An example of an automated Cleveland open-cup flash point apparatus. (Courtesy of Petroleum Analyzer Corp.)

detection of the flash point, and the recording of the flash point.

TESTERS OPERATING ON A DIFFERENT PRINCIPLE

General Comments

There are two flash point testers in general use that are of more recent origin than the manual apparatus described previously. These are an instrument called both the Setaflash apparatus and the small-scale apparatus, and the most recent addition to the flash point pantheon, the CCCFP apparatus.

Figure 4.12—An example of an automated Abel closed-cup flash point apparatus. (Courtesy of Petrotest Instruments.)

Figure 4.13—An example of an automated Tag closed-cup flash point apparatus. (Courtesy of Tanaka Scientific.)

Figure 4.14—An example of an automated Pensky-Martens closed-cup tester. (Courtesy of Petroleum Analyzer Corporation.)

Both of these use a somewhat different system than the earlier models of flash point tester described above. The small-scale (formerly referred to as Setaflash) apparatus is designed to provide thermal equilibrium at the temperature control point and requires a separate sample of 2 mL (for the low-temperature model) or 4 mL (for the high-temperature model) for each temperature tested. The CCCFP apparatus tests for a flash point at gradually increasing temperatures but keeps the lid on the test cup and, after each ignition trial, introduces about 1.5 mL of air into the test cup so there will be enough oxygen present for the next trial. The CCCFP apparatus senses a sudden increase of pressure in excess of 20 kPa above atmospheric that occurs within 100 ms of the application of the ignition source if a flash occurs. Additional details of the two types of apparatus follow.

The Small-Scale Closed Tester

The core of the small-scale tester (Figures 4.15 and 4.16) consists of an aluminum or other nonrusting metal block 61.5–62.5 mm in diameter containing a cylindrical sample cup 49.4–49.7 mm in diameter and 9.70–10.00 mm deep. This block is fitted with a cover containing an opening slide, a sample injection orifice, and an ignition flame mechanism. The metal block contains a thermometer hole and thermometer; an electrical heater is attached to the block. The electrical heater is controlled by a system that controls the equilibrium temperature within ±0.5°C (±1°F) for low-temperature testing or within ±2.0° C (±4°F) for high-temperature testing. The apparatus is also equipped with an audible signal that is given after 1 min in the case of low-temperature testing (ambient to 100°C) or after 2 min in the case of high-temperature testing (100–300°C). Additional dimensions and details are provided in STM D3278 and D3828 and in ISO 3679 and ISO 3680[6–9].

A test (ignition) flame approximately 4 mm in diameter and a pilot flame to maintain the test flame are provided on the cover. A gage ring 4 mm in diameter is engraved on the cover near the test flame to aid in obtaining the correct flame diameter. When activated, the test flame nozzle intersects the plane of the underside of the cover. Various gas sources are suggested for the flames, including piped gas or liquefied petroleum gas (ASTM Test Method D3278) and an external propane supply or an attached tank of butane (ASTM Test Method D3828).

No specifications are given in either ASTM Test Methods D3278 or D3828 for the thermometers that are the mercury-in-glass type. ASTM Test Method D3278 refers to low-, medium-, and high-temperature types and instructs the user of the standard to test the thermometers to determine that scale error does not exceed 0.25°C (0.5°F). The use of a magnifying glass is suggested to assist in making temperature observations. The two ISO standards provide specifications for a subzero (−30° to +100°C), a low-range (0–110°C), and a high-range (100–300°C) thermometer. Scale divisions are given as 1°C for the first two and 2°C for the last, with maximum scale errors of 0.5°C and 2.0°C, respectively. The total length of each thermometer is given as 195–200 mm with immersions of 44 mm and bulb diameters of 4–6 mm for all three thermometers. IP (Energy Institute) thermometers IP 91C and IP 98C are said to meet the requirements of the low-range and the high-range thermometers, respectively, but no IP thermometer was referenced for the subzero range. An alternative temperature measuring device or system of equivalent accuracy was permitted by the ISO standards.

The CCCFP Tester

ASTM Test Method D6450 shows that the core of the CCCFP (continuously closed flash point) tester (Figures 4.17, 4.18, and 4.19) is a test chamber consisting of a 4-mL sample cup made of nickel-plated aluminum (or other material of comparable heat conductivity) and a temperature-controlled brass lid [10]. Two temperature sensors to measure the specimen and the lid temperatures, two electrically insulated pins for a high voltage arc, and a connecting tube for pressure monitoring and air introduction are incorporated in the lid design. Associated equipment include a system for electronically controlling the lid temperature and providing a digital readout of the specimen temperature. Located outside the sample cup is a magnet rotating at 250–270 rpm and driving a small stirring magnet that is inserted into the cup after the sample has been introduced.

The 4-mL sample cup (Figure 4.18) has a diameter of about 30 mm where the cup contacts the lid, but this tapers to a diameter of about 21 mm some 5 mm below the top. The depth of the cup is about 15 mm and the surface of the 1-mL sample after the stirring magnet has been inserted is approximately 11.5 mm below the point of contact with the lid. The stainless steel arc pins extend about 5.5 mm below the under surface of the lid into the cup space. The gap between the two arc pins is about 2.5 mm, and the energy of the high voltage arc that is released between the pins is about 3 mJ (3 Ws) per arc. This energy is discharged between the pins in 41 ms or less. The specimen temperature sensor is a thermocouple (nickel-chromium/nickel, or similar) in a 1-mm diameter stainless steel tube that penetrates 2–2.5 mm into

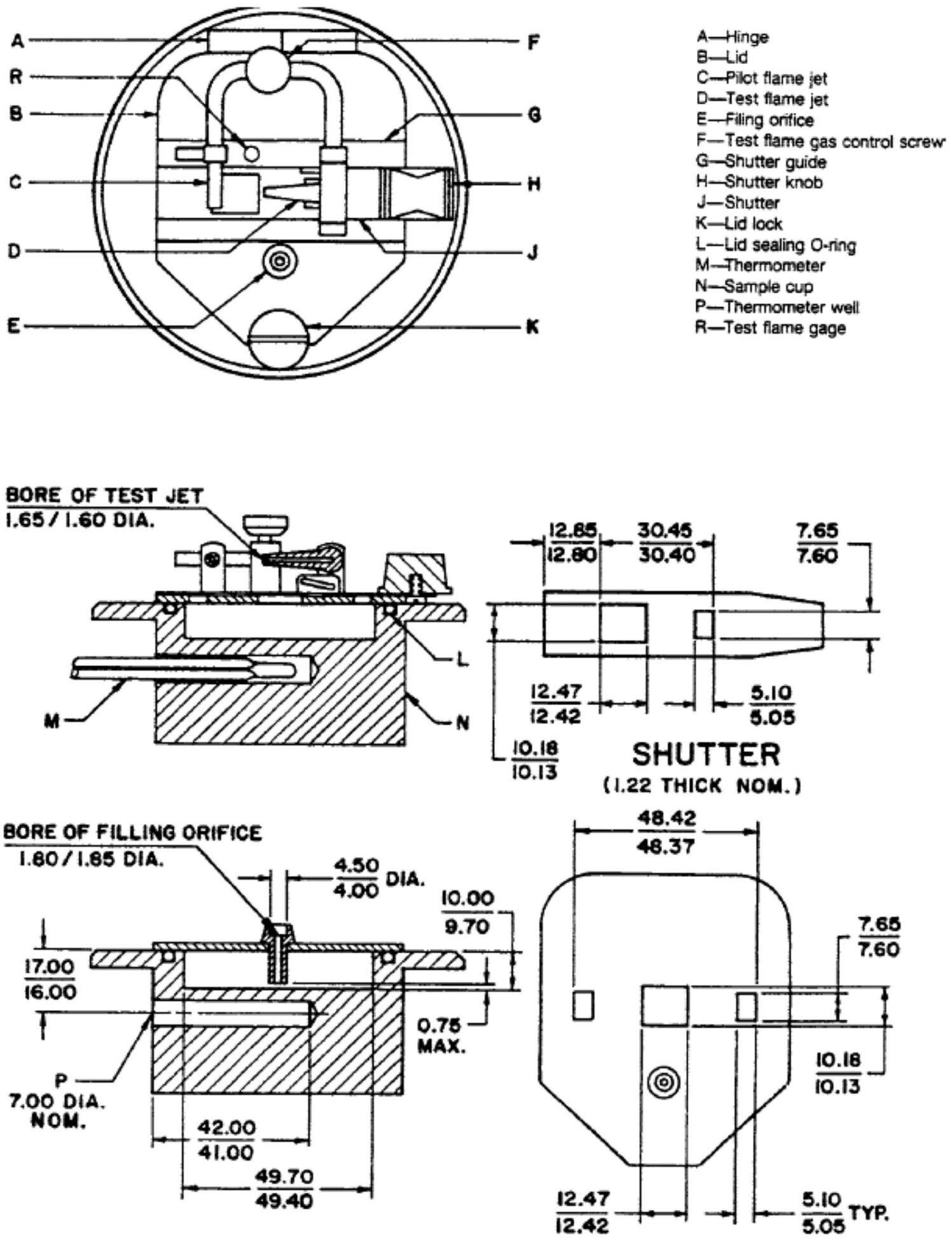


Figure 4.15—Schematic of small-scale closed-cup tester. (Courtesy of ASTM International D3828.)

the test specimen. The t (90) response time of the thermocouple is 3 s. This system has a resolution of 0.1°C and a minimum accuracy of ±0.2°C, preferably with a digital readout. Electrical-heating and thermoelectric-cooling systems are provided for controlling the lid temperature within 0.2°C.

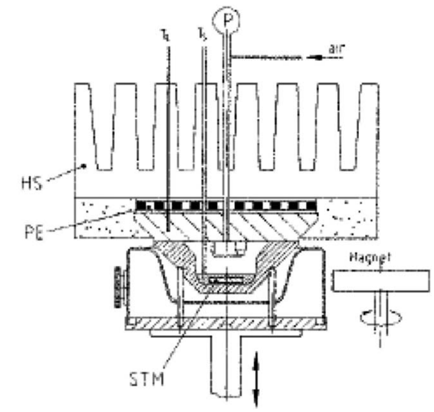
A pressure transducer is provided to sense when a flash occurs and this transducer is capable of detecting an instantaneous pressure increase above atmospheric pressure of as little as 20 kPa within 100 ms. Automatic correction of the flash point temperature to a sea level standard pressure of 1 atm can be incorporated into the system. A modification of the ASTM Test Method D6450 in 2004 lead to the MCCCFP (modified continuously closed-cup flash point tester) with the designation ASTM Test Method D7094 [11]. It uses essentially the same apparatus as ASTM Test Method D6450 but uses a 2-mL specimen size, a 7-mL cup size, and a heating rate of 2.5 mL/min.

AUXILIARY APPARATUS

General Glassware and Measurement Devices

Conducting a flash point determination requires various pieces of common laboratory glassware in addition to the flash point apparatus, e.g., for cooling, transfer, and measurement. For measurement, these include such items as various sizes of graduated cylinders, pipettes, and syringes. These may or may not be listed in the various standards. An example of a standard that does specify at least some of the glassware requirements is ASTM Test Method D6450, which indicates that introduction of the test portion of 1.0 ± 0.1 mL into the CCCFP chamber shall be accomplished by the use of a pipette or syringe of the required accuracy. Similarly, ISO 3679 specifies the use of a 2-mL syringe for introducing a 2-mL size test specimen and a 5-mL syringe for introducing a 4-mL test specimen. As described previously, some of the old types of manual apparatus had systems for ensuring

Figure 4.16—An example of a manual small-scale closed-cup tester. (Courtesy of Koehler Instruments.)



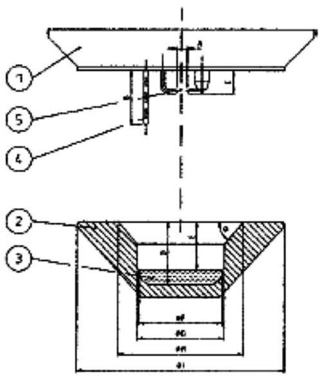
TL	Lid temperature sensor	HS	Heat sink
TS	Sample temperature sensor	PE	Peltier element
Air	Air inlet	Magnet	Rotating magnet
P	Pressure transducer	STM	Stirring magnet

Figure 4.17—The CCCFP chamber assembly. (Courtesy of ASTM International D6450.)

standard sizes of test specimen that were part of the apparatus design. Therefore, anyone conducting a standard flash point test should be careful to follow the specific instructions of the standard.

Barometer

Because flash point tests may be conducted at various altitudes and thus under various ambient atmospheric pressures, the various flash point standards regularly call for a correction of the observed flash point temperature to the standard sea level pressure of 101.3 kPa. At one time, the mercury barometer, which provides the atmospheric pressure in terms of the height of a mercury column, was a common sight in laboratories devoted to chemical or physical measurements. The normal sea level atmospheric pressure would be 760 mm of mercury at 0°C or 29.921 in. of mercury. Corrections to the reading are needed to compensate for the temperature of the mercury. For greater accuracy, other corrections may be required, e.g., a correction for the variation of gravity with altitude and latitude. The Fortin type of barometer is a form of mercury barometer.



1 Lid with incorporated temperature sensor and electric heating, made of brass.
2 Sample cup, made of nickel-plated aluminum.
3 1 mL specimen.
4 Specimen temperature sensor (NiCr-Ni thermocouple).
5 Arc pins, made of stainless steel. Arc gap of defined length.

Designation	mm
A	2.5 ± 0.2
B	14 ± 0.3
C	5.5 ± 0.2
D	15 ± 0.5
E	11.5
F	20
G	21
H	30
I	50
α	45°

NOTE—Finish of the metal to metal contact surfaces of lid and sample cup: 30 microns.

Figure 4.18—Details of CCCFP lid and cup assembly. (Courtesy of ASTM International D6450.)

Figure 4.19—An example of a CCCFP flash point apparatus. (Courtesy of Grabner Instruments.)

Figure 4.20—An example of a flash point instrument with an automatic sample changer. (Courtesy of Petroleum Analyzer Corporation.)

The aneroid barometer does not use a column of mercury but, rather, depends on the deflection of a diaphragm when there is a difference of pressure on its two faces. The diaphragm is frequently metallic, and very delicate instruments can be made by using electrical or optical methods for amplifying the movement of the diaphragm. Occasional calibration may be needed if accuracy is critical.

All the ASTM and ISO standards warn against using aneroid barometers such as those used in weather stations and airports that are precorrected to give sea level readings. None of the ASTM Standard Test Methods specify the barometer in detail, but ISO specifies the use of either a Fortin type or other suitable type of barometer readable to, and with an accuracy of 1 hPa. (Note: 1 hPa is equivalent to 0.1 kPa.)

Automatic Sample Changers

Some models of automated flash point apparatus can be furnished with automatic sample changers such as shown in Figure 4.20. This allows six or more different samples to be made ready for introduction into the flash point apparatus. Once such system has been set up, the flash point determination requires very little of the operator's time for an extended period. One technique used by such apparatus is to fill a series of test cups with the various samples. Then, the next test cup with sample is moved into place when the previous test cup with sample has given a flash point result and has been removed automatically from the flash point apparatus. Such a system can yield a significant savings of operator time if care is taken to prevent loss of volatile components while the cup and sample is in the waiting stage.

CHAPTER SUMMARY

Many designs of open-cup and closed-cup flash point apparatus were developed when man first became concerned about the potential fire and explosion hazards of volatile materials. These early manual designs were essentially simulations of two real-life situations, i.e., spillage in an open area and spillage in a confined area. In the English-speaking countries and in many other parts of the world, only a few designs have survived and been standardized. Of the open-cup flash point variety, only the Cleveland open-cup and the Tag open-cup testers have survived. Of the closed-cup variety, only the Abel, Pensky-Martens, and Tag closed-cup testers survive.

Both the open-cup and the closed-cup flash point testers cited above required large volumes of sample relative to the two modern flash point testers. The open-cup testers required about 90 mL for the Tag and about 75 mL for the Cleveland, whereas the closed-cup testers required volumes ranging from about 50 mL for the Tag to about 70 mL for the Pensky-Martens. The modern designs need only from 1 mL to 4 mL of test specimen.

The sample cups of the early flash point testers were usually made of brass, although the Tag open-cup tester used a glass sample cup. The small-scale (Setaflash) apparatus has its cup in the aluminum block that also serves as a heat sink. The CCCFP apparatus uses a nickel-plated aluminum cup.

The early testers used an open flame as the ignition source and the standards for these testers still call for the use of gas flames, with electric igniters as an alternative. The modern small-scale tester also specifies a gas flame, but the CCCFP and MCCCFP apparatus uses a high-energy spark.

In the early testers, the distance from the surface of the test specimen to the ignition flame ranged from a minimum of 6 mm in the Tag open-cup tester to a maximum of about 29 mm in the Tag closed-cup tester. In the two modern testers, it ranges from about 6 mm in the CCCFP tester to about 9 mm in the small-scale tester using the 2-mL sample size.

Table 4.1 below summarizes some of this information. Additional dimensions and details are provided in the individual standards.

TABLE 4.1—Summary of Sample Volumes, Surface to Ignition Source Distances, and Other Details for Various Testers

Tester and Type	Approx. Sample Size, mL	Surface to Ignition Distance, mm	Stirring	Cup Material
Open Cup				
Cleveland	75	12	None	Brass
Tag	90	6	None	Glass
Closed Cup				
Abel	78	18	30	Brass
Tag	50	29	None	Brass
Pensky-Martens	70	22	120/250	Brass

TABLE 4.1—Summary of Sample Volumes, Surface to Ignition Source Distances, and Other Details for Various Testers (Continued)

Tester and Type	Approx. Sample Size, mL	Surface to Ignition Distance, mm	Stirring	Cup Material
Newer Types				
Small-Scale	2/4	9/8	None	Aluminum (Al)
CCCFP (MCCCFP)	1	6	260	Nickel-plated Al

REFERENCES

[1] ASTM D92, "Standard Test Method for Flash and Fire Points by Cleveland Open Cup Tester," *Annual Book of ASTM Standards,* ASTM International, West Conshohocken, PA.

[2] ASTM Dl310, "Standard Test Method for Flash Point and Fire Point of Liquids by Tag Open-Cup Apparatus," *Annual Book of ASTM Standards,* ASTM International, West Conshohocken, PA.

[3] ISO Standard 13736, "Petroleum Products–Determination of Flash Point–Abel Closed Cup Method," International Organization for Standardization, Geneva, Switzerland, 1994.

[4] ASTM D56, "Standard Test Method for Flash Point by Tag Closed Cup Tester," *Annual Book of ASTM Standards,* ASTM International, West Conshohocken, PA.

[5] ASTM D93, "Standard Test Method for Flash Point by Pensky-Martens Closed Cup Tester," *Annual Book of ASTM Standards,* ASTM International, West Conshohocken, PA.

[6] ASTM D3278, "Standard Test Method for Flash Point of Liquids by Setaflash Closed Cup Apparatus," *Annual Book of ASTM Standards,* ASTM International, West Conshohocken, PA.

[7] ASTM D3828, "Standard Test Method for Flash Point by Small Scale Closed Tester," *Annual Book of ASTM Standards,* ASTM International, West Conshohocken, PA.

[8] ISO Standard 3679, "Determination of Flash Point–Rapid Equilibrium Closed Cup Method," International Organization for Standardization, Geneva, Switzerland, 1983.

[9] ISO/DIS 3680, "Determination of Flash/No Flash–Rapid Equilibrium Closed Cup Method," International Organization for Standardization, Geneva, Switzerland," 1983.

[10] ASTM D6450, "Standard Test Method for Flash Point by Continuously Closed Cup (CCCFP) Tester," *Annual Book of ASTM Standards,* ASTM International, West Conshohocken, PA.

[11] ASTM D7094, "Standard Test Method for Flash Point by Modified Continuously Closed Cup (MCCCFP) Tester," *Annual Book of ASTM Standards,* ASTM International, West Conshohocken, PA.

5

Sampling and Test Specimens

INTRODUCTION

This chapter examines the processes required to ensure the acquisition of a representative sample and test specimen for use in flash point determinations. An old axiom states that no test result is better than the sample on which the test is run, and that axiom holds true for flash point determinations. If a sample is not representative of the lot of material from which it is drawn, or if the sample is contaminated or has degraded in any way during its trip to the laboratory where the flash point determination is to be made, the result is at best misleading.

The strategy for obtaining a representative test specimen for a flash point determination depends upon a number of factors. The sampling technique depends first of all on whether the bulk material is in a tank, barge, ship, rail car, tank truck, or pipeline. It also depends on whether the testing laboratory is close to the sampling site or whether the sample must be shipped for many miles, and on whether there is close liaison between the testing laboratory and the original sampling crew or whether they too are separated by many miles. Another factor to consider is whether the sample is a dedicated sample for use solely in the flash point test or whether flash point is one of many tests to be run on a bulk sample. It is also important to take into account whether the flash point determination is likely to be run immediately after receipt of the sample or whether there will be a delay of hours or even days. Finally, consideration must be given to the properties of the material such as its volatility and its flammability classification, as well as whether the material is a uniform solution or a multiphase suspension. In the latter case, care must be taken that the suspended material is present in representative amounts in the sample.

When a laboratory receives a sample that is to serve for many determinations as, for example, when a petroleum fuel sample is to be tested for compliance with a specification, the order in which the tests are run becomes important. If volatile components are present and if tests depending on volatility are to be run, those tests should be run before other tests that do not depend on volatility. That means that the flash point test should be run early, preferably first, before volatile components are lost by repeated opening and closing of the sample container. (Of course, those who have to run vapor pressure or distillation tests will also think they should be first, but that is a matter to be determined by the laboratory supervision.)

TERMINOLOGY

ASTM Practice D4057 on manual sampling defines "sampling" as all the steps required to obtain a sample that is representative of the contents of any pipe, tank, or other vessel and to place that sample in a container from which a representative test specimen can be taken for analysis [1]. A "representative sample" is defined as a portion extracted from the total volume that contains the constituents in the same proportions that are present in the total volume. For example, it is a portion of the contents of a tank, barge, or tank car that contains all the components of those contents in the same proportions as in the whole of the contents. A "sample," however, is merely a portion extracted from a total volume that may or may not contain the constituents in the same proportions that are present in that total volume. In short, all samples are not representative samples.

ASTM Practice D4177 on automatic sampling provides us with the definitions of some additional terms [2]. An "automatic sampler" is a device used to extract a representative sample from the liquid flowing in a pipe and an "automatic sampling system" encompasses not only the automatic sampler but also any stream conditioning and mixing and handling involved in obtaining the sample. "Isokinetic sampling" is sampling conducted in such a manner that the linear velocity through the opening of the sample probe is equal to the linear velocity in the pipeline at the sampling location and is in the same direction as the bulk of the liquid approaching the sampling probe. There are two basic types of samples taken by automatic sampling systems. A "flow proportional sample" is one taken at a rate that is proportional to the flow rate in the pipe throughout the sampling period. A "time proportional sample" is one composed of equal volume grabs taken from a pipeline at uniform time intervals during the entire transfer. (ASTM Practice D5842 refers to the flow proportional sample as a "flow-responsive proportional" type of sample and the latter as a "time cycle non-proportional" type of sample [3].) The vessel into which all samples are initially collected is called the "primary sample receiver."

ASTM Practice D5854 defines two other terms of general application [4]. The vessel into which a sample is initially collected is called the "primary container," and any vessel into which all or part of the sample from a primary container is transferred for transport, storage, or ease of handling is called an "intermediate container." For example, if a seller takes a sample from a shipment and splits it between the buyer's laboratory and his own laboratory, he would be transferring it from the primary container into intermediate containers.

For the discussions in this chapter, certain terms will be used in a general but consistent sense. "Field sample" will be used to indicate any sample prior to its receipt by the testing laboratory. It may indicate a sample of a planned shipment from the manufacturer who may be many thousands of miles from the laboratory, or it may be used to indicate a sample from a tank car of material sitting on a siding within feet of the testing laboratory. "Laboratory sample," or "lab sample" for short, will be used to indicate a field sample once the laboratory has received and taken custody of it. The term will refer both to the full sample as received and to what remains of the sample after one or more portions have been removed for conducting tests.

The ASTM publication “Form and Style for ASTM Standards” defines a “test unit” as a unit or a portion of a material that is sufficient to obtain a test result(s) for the property or properties to be measured. The same document defines a “test specimen” as a test unit or portion of a test unit upon which a single or multiple observation is to be made. Both a “test unit” and a “test specimen” are frequently referred to as “subsamples” or “aliquots” of the lab sample.

SAMPLE SCENARIO

The sampling history between the bulk material and the test specimen will be assumed to conform more or less to a common scenario. A field sample is obtained and transported to a testing laboratory. The laboratory takes custody of the sample, stores it until someone can begin tests, conditions the sample prior to subsampling (temperature adjustment, mixing, etc.), obtains subsamples, and conducts tests.

The discussion of sampling and of obtaining subsamples for test specimens that follows draws extensively on the previously mentioned standard sampling practices that have been developed by ASTM Committee D02 on Petroleum Products and Lubricants. Because every material or industry presents its own problems, these discussions are intended only as a framework, an indication of some of the factors that must be taken into account when designing the sampling and testing program. Comparable sampling practices are available from the American Petroleum Institute (API), the ISO, the EI (IP), and other standards organizations [5]. Government regulations such as those of the U.S. Department of Transportation (DOT) must also be considered.

TAKING THE FIELD SAMPLE

General

It cannot be emphasized too strongly that each sampling situation must be examined separately, and the sampling protocol must be established on the basis of information on the physical conformation of the tank, pipeline, or other container and upon the physical and chemical nature of the substance to be sampled. The following overview of possible approaches is based on sampling practices standardized by ASTM Committee D02 on Petroleum Products and Lubricants. These are brief summaries, so the original standard practices should be consulted for details.

Preparation of Sampling Equipment

To preclude contamination of the field samples, all equipment used in taking the sample and all containers in which the samples are collected must be free of dirt or other deposits. ASTM Practice D4057 specifies that the sampling equipment be clean prior to commencing the sampling operation as any residual material left in a sampling device or sample container from a previous sample or cleaning operation may destroy the representative character of the sample [1]. Another practice, ASTM Practice D5842, similarly instructs that sampling apparatus be clean, dry, and free of any substance that might contaminate the sample [3].

Selection and Preparation of Sample Containers

ASTM Practice D4057 suggests that it is good practice when sampling light petroleum products to rinse the container with the product to be sampled prior to drawing samples. The practice further instructs that any sampling bottle, beaker, graduated cylinder, or sampling container used during sampling be inspected for cleanliness and used only if clean and dry.

ASTM Practice D4177, which covers automatic sampling of petroleum products, warns that if loss of vapors will significantly affect the analysis of the sample (as such loss would in the case of flash point determinations), then a variable volume type receiver should be considered [2]. This practice further warns that the materials of construction for the receiver should be compatible with the petroleum product sampled.

ASTM Practice D5842, which covers sampling for volatility measurements, lists three types of sample containers, specifically, clear or brown glass bottles, fluorinated high-density polyethylene bottles, and metal cans [3]. Clear glass bottles are easily examined visually for cleanliness and allow inspection of samples for the presence of free water or solid impurities. Brown glass bottles provide some protection from light that sometimes induces oxidative deterioration evidenced by a color change in the sample. Cans are acceptable only when their seams are soldered on the exterior surface.

ASTM Practice D5842 recommends corks or screw closures for bottles, and only screw caps with inserted seals for cans. Corks should, of course, be clean and free of holes and loose bits of cork. To prevent contact of the sample with the cork, tin or aluminum foil should be wrapped around the cork. Rubber stoppers are absolutely forbidden. However, ASTM Practice D5842 applies to petroleum products that can attack rubber, so such stoppers may be suitable for other types of samples.

ASTM Practice D5842 also specifies that, before reusing the sample container, it should be washed with strong soap solution, rinsed thoroughly with tap water, and finally with distilled water. It must then be dried completely and stoppered or capped immediately. In short, any container must be absolutely clean and free of foreign matter.

This same practice provides guidance on labeling samples. It states that the container should be labeled immediately after the sample is obtained, using waterproof and oilproof ink, or a pencil hard enough to dent the tag. Typical label information would include such information as:

- the date and time the sample was taken;
- the name of the sample;
- the location where the sample was taken;
- the identification of the owner of the vessel or container;
- the brand and grade of material;
- an identification number;
- other information required by federal, state, or local regulations.

Sampling Marine Cargoes

Marine cargoes in tankers and barges are addressed for crude oils by Practice D4057. Several ways for obtaining a custody transfer sample are suggested, specifically, from the shore tanks before loading and both before and after discharging; from the pipeline during the discharging or loading; or from the ship’s or barge’s tanks after loading or before discharging. Normally, the shore tank sample before loading or the pipeline sample taken from the loading line is the custody transfer sample.

For ship or barge cargoes of finished petroleum products, ASTM Practice D4057 states that samples are taken from both shipping and receiving tanks and from the pipeline. In addition, it is suggested that the product in each of the ship or barge tanks be taken just after the ship or barge is loaded or just before product is discharged. In addition, Chapter 17 of an API publication is suggested for additional guidance [5].

In planning a sampling protocol for any ship or barge cargo, consideration must be given to several factors. First, it should be recognized that there is a potential for product contamination from condensed moisture from the humid air over oceans and other waterways. Second, the irregular shapes of ship and barge tanks means varying volumes are present at different depths. Finally, exposed structural members in such tanks can act as traps for condensed water or for the residues of previous cargoes.

Tank Sampling

Storage tanks can be of various shapes and made of various materials. For the purposes of the following discussion, the term "tank" is limited to those designs that are fundamentally right circular cylinders made of steel or other metal, with or without protective coatings, and with various internals and attachments. In many cases, sloping bottoms leading to a discharge connection may be present.

Tanks come in many sizes from research or pilot plant tanks holding only a few liters to huge tanks at petroleum refineries holding well in excess of a thousand barrels (42,000 gal) of crude or product. When the contents of a tank are of uniform composition, a sample taken from any part of the tank would be representative. However, when multiple phases are present, such as water bottoms in a petroleum tank or multiple fuel layers when incompatible fuels have been placed in the same tank, care must be taken in the sampling procedure. For small tanks, simple circulation of the contents may suffice to produce contents that are uniform throughout the tank but uniformity is much more difficult to obtain by circulating the contents of large tanks because size and internals tend to produce dead spaces that the flow of liquid does not reach. ASTM Practice D4057 provides guidance on alternative sampling procedures.

Samples should not be taken from within solid standpipes because the material in the standpipe is normally not representative. A standpipe is a section of pipe or tubing extending from the gauging platform of a tank to near the bottom of tanks equipped with internal or external floating roofs. Standpipes may also be found in the tanks of ships or barges. Standpipe samples should only be taken if the standpipe contains at least two rows of overlapping slots.

For tanks with diameters greater than about 45 m or 150 ft, samples taken at a single gauging hatch are inferior to multiple samples taken at additional hatches located around the tank perimeter, if such sampling locations are available. Each of the multiple samples should be analyzed and the results averaged arithmetically.

Composite samples (blends of spot samples) from crude oil tanks are taken by the three-way method or, for tanks smaller than 1000 barrels containing 3–4.5 m (10–15 ft) of crude, the two-way method may be used. In the three-way method, equal volume spot samples are taken at the upper, middle, and lower or outlet connection of merchantable oil. In the two-way method, equal volume samples are taken from the upper and lower, or outlet connection of merchantable oil.

Various devices have been developed for obtaining spot samples. A core thief sampler may be used for sampling liquids whose Reid vapor pressure is 101 kPa (14.7 psia) or less. (See Practice D4057 for a typical design.) A bottle or beaker procedure may also be used for sampling such liquids or sampling solids or semisolids that can be liquefied by heat. The bottle or beaker is weighted or, preferably, fitted into a sampling cage. A cork or stopper in the bottle or beaker is removed when the bottle or beaker has reached the desired liquid depth.

Running or all-level sampling is sometimes attempted using stoppered bottles or beakers. The goal in such a sampling procedure is to obtain equal volumes from all tank levels as the bottle or beaker is raised through the liquid. However, such samples are not always representative because the rate of filling is proportional to the square root of the depth of immersion, thus requiring a variable rise rate that the operator may not be able to accomplish.

Tanks may be equipped with taps having a minimum diameter of 1.25 cm (1/2 in.) if light products are involved or a minimum of 2.0 cm (3/4 in.) if heavy, viscous liquids are involved. The use of taps assumes, of course, that the tank contents are uniform.

Sampling Horizontal Tanks and Rail Cars

Some tanks are horizontal cylinders with dished ends. Such tanks may be found as underground tanks, as aboveground tanks, as railroad tank cars, or as tank trucks. Some of these tanks may be divided into compartments or may be baffled to dampen any sloshing of liquid. If the contents are uniform in composition, almost any type of sample will be representative. Otherwise, care must be taken to incorporate consideration of the variable volume per unit of depth in the sampling plan. The running or all-level sample mentioned above will definitely not provide a representative sample. Sometimes, too, horizontal tanks are not level. Tanks at fixed locations may be installed with a slight slope so that condensed water (in petroleum product tanks) will collect at the lower end for ease of removal. Railroad tank cars and tank trucks may be parked on a sloping section of track or on sloping ground, respectively. Such slopes may result in nonuniform distribution of nonhomogeneous product from one end to the other. Additional difficulties may be imposed by a limited number of access points along the length of the tank. The sampling protocol must take such factors into consideration. The most representative sample for tank cars or tank trucks may be those obtained from the loading or discharge lines while the tanks are being filled or as the contents are being discharged upon delivery.

Sampling Drums, Barrels, and Cans

Some products are not shipped in bulk but, rather, in package lots consisting of cans, drums, barrels, or boxes. In such cases, a sufficient number of the packages are selected randomly to prepare a composite sample that is representative of the lot and sufficiently large for the number of tests and analyses to be conducted. ASTM Practice D4057 notes that the number of packages selected will depend on various factors such as the uniformity of quality from package to package, the sources and type of material, and whether it represents one or more production lots, and the tightness of the product specification.

Pipeline Sampling

Circumstances sometimes dictate obtaining samples from flowing streams in a pipeline rather than from tanks and other containers. Such things as lack of sampling openings, extensive and interfering tank internals, or odd-shaped tanks may make pipeline sampling during product transfer a convenient alternative to tank sampling. Pipeline sampling can be accomplished manually as discussed in ASTM Practice D4057 or automatically as discussed in ASTM Practice D4177.

If the liquid or semiliquid being sampled has a Reid vapor pressure of 13.8 kPa (2 psia) or less and if there is an open discharge stream of relatively low flow as from small filling and transfer pipelines (5-cm or 2-in. diameter or less), the dipper sampling technique may be used. The dipper should have a flared bowl with a handle of convenient length and should be made of a material that will not affect the product being sampled. (ASTM Practice D4057 suggests tinned steel for petroleum products.) The dipper capacity should be suitable for the amount to be collected. The dipper, like any other sampling device, must be kept clean and dry and free of any dust or dirt. Dipper samples are taken from the full cross section of the flowing stream at time intervals selected so the total composite sample is proportional to the pumped quantity.

When the liquid has a greater Reid vapor than the 13.8 kPa cited above, or a larger flow, a method using probes may be used, e.g., for liquids of 101 kPa (14.7 psia) RVP or less and semiliquids in pipelines, filling lines, and transfer lines. ASTM Practice D4057 shows three types of probes suitable for diverting a sample from the flowing stream, specifically, a tube beveled at a 45° angle; a probe with a short radius elbow or pipe bend; and a closed tube with a round orifice near the closed end. All probes must extend into the center third of the pipe's cross-sectional area with their inlets facing upstream. Since, in sampling petroleum products, the fluid may contain water or heavier particles, the selection of the location, position, and size of the probe must be such as to minimize any separation of the alien particles. (As a young engineer, the author was instructed to keep the flow velocity in the probe the same as it was in the portion of the stream being sampled.) The probe should preferably be in a vertical section of the pipeline, if such a section is available, but may be located in a horizontal section if the flowing velocity is sufficient to provide turbulent conditions. Otherwise, a system for mixing should be installed upstream from the probe. Such mixing systems may consist of a section of reduced diameter pipe, a series of baffles or orifices or perforated plates. The probe system should include a valve to control the rate of sample withdrawal. That rate should be roughly the same as the linear velocity at the probe opening. This implies a means of measuring the flows in both the pipeline and the probe.

When custody transfer is involved, continuous automatic sampling, rather than the manual sampling described above, is preferred. Such automatic sampling of petroleum and petroleum products with Reid vapor pressures at sampling and storage temperatures less than or equal to 101 kPa (14.7 psia) is covered by ASTM Practice D4177. This practice is an extremely detailed guide to the varied aspects of automatic pipeline sampling. In fact, it is too detailed to include anything but a brief summary below of the major points, so it is essential that anyone wishing to use an automatic pipeline sampling system refer to the original document.

An automatic sampling system must perform several distinct tasks. First, the system must condition the material to be sampled. For example, free water entrained in an oil must be homogenized. Obviously, this task must be performed upstream of the sampling location. Second, there must be a flow measurement device for flow proportioning. Third, there must be a means for controlling the total volume of sample extracted. Fourth, there must be a sample receiver to receive and store the sample without altering the sample composition. This means, among other things, that venting of vapors during receiver filling and storage must be minimized. This is particularly important when the sample is to be used for tests where volatility is important, such as flash point, vapor pressure, and distillation determinations. Finally, the properties of the material may necessitate insulation, heating, or both for individual components of the system or for the full system.

Every grab (the volume of sample extracted from the pipeline by a single actuation of the sample extractor) must be taken in proportion to flow. However, if the flow rate during the total delivery varies by less than 10 % from the average flow rate, a representative sample may still be obtained by time proportional control of the grabs. There are two major types of automatic sampling systems. One locates the extracting device directly in the main line, whereas the other locates the extracting device in a sample loop.

The three types of probes used in manual sampling of pipelines are also specified for automatic sampling. The extractor (a device that extracts a sample from the flowing stream) may or may not be an integral part of the probe. Regardless of its location, the extractor should extract a consistent volume repeatable over the range of operating conditions and sampling rates. The sampling controller, which governs the operation of the extractor, should permit the selection of sampling frequency. Acceptance testing of automatic samplers is recommended to confirm that the system is performing accurately. Such acceptance testing may test either the total system or the individual components. Once a system has been proven, checks should still be made from time to time to confirm system reliability.

Sampling Solids and Semisolids

Although we normally think of flash points being run on materials that are liquid at ambient temperature, there are some solids and semisolids on which flash point determinations are made. For example, flash points may be determined on waxes, asphalts, industrial wastes, cosmetic gels, heavy residual fuels, greases, and similar materials. In some cases, sampling may be accomplished by first liquefying the substance by heating and then using any applicable liquid sampling technique. However, there are also techniques for sampling the materials without first liquefying them. ASTM Practice D4057 describes techniques called tube sampling and boring sampling as well as a technique for sampling grease.

The tube-sampling technique is suitable for sampling liquids of 13.8 kPa (2 psia) Reid vapor pressure or less and for sampling semiliquids, in drums, barrels, and cans. The apparatus used consists of either a glass or metal tube that will reach to within 3 mm (1/8 in.) of the bottom of the container. For sampling a barrel or drum, the tube should hold 500 mL to 1 L (roughly 1 pt to 1 qt). The drum or barrel is placed on its side if it has a side bung or sampled in the upright position if it has a head bung. The tube is rinsed with the product before taking a sample by closing the tube with the thumb and lowering it into the drum to a depth of about 30 cm (1 ft). The thumb is then removed to allow material to flow into the tube. The thumb is again used to seal the upper opening of the tube, and the tube is withdrawn. The contents are then allowed to flow to all parts of the tube to rinse it before that rinse material is discarded.

To obtain an all-levels sample, the tube is inserted to the bottom of the drum but with the upper opening unsealed. The thumb is placed over the upper opening, the tube is removed, and the sample is transferred to the sample container. Smaller tubes are used for sampling cans of smaller volume.

The boring-sampling technique is used for sampling waxes and soft solids in barrels, cases, bags, and cakes when they cannot be melted and sampled as liquids. For this, a ship auger 2 cm (3/4 in.) in diameter and of sufficient length to pass through the material to be sampled is used. To obtain a sample from a barrel, for example, the head is removed, any foreign substances are removed from the surface, and three test holes are bored. One test hole is bored in the center and the other two halfway between the center and the edge of the barrel. The three borings are placed in individual sample containers so that, on delivery to the laboratory, they are examined individually (if there are visual differences) or combined for a single determination. Subdivision of the sample to test specimen size can then be accomplished by mixing and quartering techniques.

Because a wide variety of situations can be encountered, ASTM Practice D4057 provides only general guidance for the sampling of production lots or shipments of lubricating grease and of soft waxes and bituminous materials similar to grease in consistency. The guidelines are probably equally applicable to cosmetic products or other products of similar nature. First, samples should not be taken from processing equipment and should not be taken until a grease, for example, has cooled to a temperature not more than 9.4°C (15°F) above the air surrounding the containers nor until the grease has been in the container for at least 12 h. Samples should be taken from each shipment and, if more than one production lot is involved, from each lot. The grease is examined visually at different depths and, if no visual differences are noted, samples are taken from the center about 6.5 cm (3 in.) below the center of each opened container. Note that these are general instructions, and each situation must be evaluated and a protocol established for obtaining a representative sample.

FROM FIELD TO LABORATORY

Dividing the Sample

Transporting the sample from the field to the laboratory may be as simple as walking the sample from the receiving point to the plant laboratory or as complex as shipping by truck, rail, or air for hundreds or thousands of miles. It may be as simple as taking the full sample or reducing the sample to the required size or for splitting it among two or more laboratories. However, the number of transfers using intermediate containers should be minimized. Each use of intermediate containers increases the possibility that light hydrocarbons (from petroleum and petroleum product samples) will be lost or that contaminants such as water and sediment may be lost by clinging to the sides of vessels or through inadequate mixing.

Before dividing samples, they must be homogenized to ensure that all subsamples are representative of the original material. ASTM Practice D5854 addresses means for accomplishing this for samples of petroleum or petroleum products [4]. There are two basic methods of mixing, specifically, power mixing and shaking. Power mixing in turn is divided into insertion mixing, in which the mixer is inserted into the container, and closed-loop mixing, in which the contents of the container are pumped through an external loop and back into the container. (See the Practice for acceptance criteria and acceptance testing of mixers.) As a final word of caution, remember that the substances on which flash point are to be determined are usually flammable, so equipment such as mixer drive motors should be explosion proof.

Shaking involves either manual or mechanical shaking of the container to eliminate stratification. Mechanical shaking includes bottle, can, and drum rollers as well as devices that provide a shaking motion comparable to hand shaking. Even the old practice of hand rolling a drum from one end of a room to the other end to provide agitation of its contents would be included under the shaking category. If a sample is known to be homogeneous, no mixing is, of course, needed. Also, if the analytical tests to be conducted could be affected by air entrainment from power mixing or shaking, then the samples should not be agitated.

Containers and Sample Transport

The selection of sample containers has already been discussed, but some of the main points are worth repeating. First, no single sample container type will meet the requirements for all the many types of material that may be subject to flash point testing. (Appendix X1 of ASTM Practice D5854 contains four tables showing various types of container as being suitable, preferred, not practical, or not recommended for use with crude oils, gasolines, kerosines, and fuel oils.) Furthermore, care must be taken in selecting the container material as it could affect the test results.

ASTM Practice D5854 recommends that sample containers should be large enough to hold the required volume of sample within 80 % of its total volume, to allow for thermal expansion and to facilitate mixing. Other standards provide somewhat different advice. Thus, ASTM Test Method D93 states that, for a sample of residual fuel oil, the container should be 85 to 95 full but, for other types of (petroleum) samples, the container should be not more than 85 % full nor less than 50 % full, and ISO 3679 for various paint industry materials advises that the sample container be filled to between 85 and 95 of its capacity [6,7].

Plastic containers can sometimes be attacked by the sample. For example, the plasticizer contained in the material can sometimes be leached out and contaminate the sample. Again, clear plastic that allows light transmittance may be unsuitable for the same reason as glass bottles, i.e., the light-catalyzed reactions to which some materials are susceptible.

For sample transport within one's own facility, any suitable container may be used and transported by any convenient means to the laboratory. However, where the sample must be shipped from one location to another, government regulations covering the means of shipping must be followed. For example, in the United States, any sample container containing hazardous materials or the residues of such materials that is to be shipped by air, public roadway, rail, or water, or any combination thereof, must meet requirements set forth in such regulations as those of the DOT [8]. It is incumbent upon the shipper to determine what regulations apply to the particular circumstances.

It cannot be stressed too often that only clean containers free of all substance that might contaminate the sample should be used during sampling. Prior to use, reusable containers should be rinsed with a suitable solvent, e.g., a sludge solvent in the case of petroleum products, and then washed with a strong soap or detergent solution, followed by rinsing with tap water and then with distilled or deionized water. The container must then be dried with a current of clean, warm air or by placing it in a hot (40°C), dust-free cabinet. The dried container must then be stoppered to preclude contamination prior to use.

As previously indicated, all sample containers upon filling with a sample should be adequately labeled to meet the needs of the parties concerned as well as those of government agencies such as the DOT and OSHA. As a minimum, each label should contain the name of the material; the source of the sample, e.g., the tank, barge, terminal, or pipeline from which it was obtained; the date and time of sampling; and the name of the person taking the sample.

Storage in the Laboratory

Upon receipt by the laboratory where the tests are to be conducted, the sample should be placed in a controlled storage area, not merely tossed into some unused corner until needed. As a minimum, the sample should be stored away from any sources of heat (sunlight or heating vent, for example). If prolonged storage is likely, the sample should be stored at a temperature that depends upon the nature of the sample to protect it from deterioration during the waiting period. ASTM Test Method D93 states that storage of samples in excess of 35°C or 95°F is to be avoided [6]. ASTM Test Method D6450 specifies storing in a clean, tightly sealed container at a low temperature but provides no guidance on how low the temperature should be [9]. ISO 3679 advises storing under conditions to minimize vapor loss and pressure buildup and to avoid storing at temperatures in excess of 30°C (86°F) [7]. A number of flash point standards advise against storing in plastic bottles since volatile materials can diffuse through the walls. A number also caution against use of test specimens from leaky cans because the integrity of such samples may be compromised.

OBTAINING TEST SPECIMENS AND OTHER SUBSAMPLES

Precooling and Subsampling

At this point, a field sample representative of the product or material has been taken and transported to the laboratory, where it has been stored prior to testing. If the sample is intended for evaluation by a number of test methods, e.g., a fuel sample on which specification requirements are to be evaluated, the various tests affected by loss of volatile components should be determined first. However, regardless of whether the sample is such a general sample or one dedicated to flash point determination, it will be larger than the test specimen size that is required for the flash point test.

The next task facing the analyst is that of obtaining a representative test specimen, i.e., a test specimen that has not been depleted of volatile components. The various flash point methods specify cooling the laboratory sample and the sample cup of the flash point apparatus below the expected flash point temperature. However, they differ in the extent of that cooling with the degree of cooling depending upon the type of material being tested and the expected flash point of that material.

ASTM Test Method D56 (Tag Closed Cup) specifies that both the sample and the graduated cylinder in which the test specimen is measured are to be precooled "so that the specimen temperature at the time of measurement will be 27 ± 5°C (80° ± 10°F) or at least 10°C (18°F) below the expected flash point, whichever is lower" [10]. Furthermore, it is essential that the sample temperature be maintained at least 10°C below the expected flash point during the transfers from the sample container to the graduated cylinder and from the cylinder to the test cup.

In ASTM Test Method D92 (Cleveland Open Cup), the user of the method is instructed to fill the test cup to the filling mark with both the sample and, further, that "the temperature of the test cup and the sample shall not exceed 56°C (100°F) below the expected flash point" [11].

ASTM Test Method D93 (Pensky-Martens Closed Cup) states that "the temperature of the test cup and test specimen shall be at least 18°C or 32°F below the expected flash point," and cautions against transferring material unless the temperature of the sample and of the test cup is at least 18°C (32°F) below the expected flash point temperature [6].

ASTM Test Method D1310 (Tag Open Cup) calls for a preliminary determination of the flash point, and then states, "repeat the procedure by cooling a fresh portion of the sample, the glass cup, the bath solution, and the thermometer to at least 18°F (10°C) below the approximate flash point" that was determined in the initial stages [12].

ASTM Test Method D3143 (Tag Open Cup) notes, "The test sample should be at least 11°C (20°F below the anticipated flash point" when it is placed in the test cup [13].

ASTM Test Method D3278 (Setaflash Closed Cup), cautions, "Do not open sample containers unnecessarily and do not transfer the specimen to the cup unless the temperature of the specimen is at least 20°F (11°C) below the expected flash point" [14].

ASTM Test Method D3828 (Small Scale Closed Tester) similarly states, "Do not open containers unnecessarily and make a transfer unless the sample temperature is at least 10°C (18°F) below the expected flash point" [15].

ASTM Test Method D3941 (Closed Cup Apparatus) states, "Do not make transfers unless the sample temperature is at least 20°F (10°C) below the expected flash point, except for materials that are too viscous to be handled at that temperature. In these cases, transfer the specimens at the lowest possible temperature at which the material can be accurately measured into the cup" [16].

In ASTM Test Method D6450 (Continuously Closed Cup Apparatus), the user of the method is instructed, "Do not make a transfer unless the sample temperature is at least 18°C (32°F) below the expected flash point" [9]. However, samples "of very viscous material may be warmed until they are reasonably fluid before they are tested. However, do not heat the unsealed sample above a temperature of 18°C below its expected flash point."

ISO 13736 (Abel Closed Cup) instructs the user, "Cool the sample as received, in a cooling bath or refrigerator to below −35°C, or to at least 17°C below the expected flash point, whichever is the higher, before opening the container"

[17]. The user is also advised that liquids that crystallize on cooling should be cooled to just above their crystallizing points.

ISO Standard 3679 (Rapid Equilibrium Closed Cup) specifies that subsampling to obtain a test specimen shall be conducted after cooling the laboratory sample and its container to 10°C below the first selected test temperature [18].

These various precooling requirements are summarized in Table 5.1 with the warning that there are additional details and requirements spelled out in the original documents that have been omitted in these generalized statements. Also note that, in a few cases, the Fahrenheit value precedes the Celsius value because this is the way it appeared in the ASTM Standard. Also, in some cases, the value in parentheses is not the exact conversion value. For example, in the case of ASTM Test Method D3278, the values 20°F (10°C) are shown. Such values should be interpreted as requiring 20°F below the expected flash point when operating with Fahrenheit readings or 10°C below the expected flash point when operating with Celsius readings.

Thus, precooling of a sample prior to transferring from the laboratory sample container to the test apparatus varies from a low of 10°C (18°F) below the expected flash point for many test methods to a high of 56°C (100°F) below the expected flash point for ASTM Test Method D92, the Cleveland Open Cup procedure. Care must be taken to follow the procedure exactly in this regard.

Subsampling Viscous Materials

Several of the standards also address the subsampling of highly viscous or solid samples. Thus, ASTM Test Method D92 (Cleveland Open Cup) permits the warming of very viscous material to a temperature at least 56°C (100°F) below its expected flash point. ASTM Test Method D93 (Pensky-Martens Closed Cup) also permits warming of very viscous materials "at the lowest temperature adequate to liquefy any solids" but limits the temperature to 28°C or 50°F below the expected flash point. ASTM Test Method D6450 (CCCFP) permits the warming of very viscous materials to a temperature not above 18°C below its expected flash point. ISO 3679 (Rapid Equilibrium Closed Cup) also allows heating of a sample that is too viscous at ambient temperature but limits the temperature to not more than 10°C below the test temperature. When that heating is insufficient, the sample is introduced into the test cup "with a solids dispenser or spatula . . . when the cover is open."

CHAPTER SUMMARY

Sampling and subsampling in such a way as to obtain a test specimen representative of a product is essential if a meaningful result is to be obtained. The technique to be used in field sampling is dictated by the situation, i.e., by the nature of the product, by the nature of the equipment or container from which the sample is to be taken, and by any limitations imposed by contract or legal regulations. A number of techniques described in the standard practices of ASTM Committee D02 on Petroleum Products and Lubricants have been summarized but these are intended only as illustrations of possible techniques. When the laboratory receives the field sample, a test specimen must be taken from it for each test that is to be conducted. Because loss of volatile materials from opening and closing the sample container can lead to erroneous results, flash point and other test methods where volatility is important should be conducted first. Cooling of the sample container and sample to temperatures below the expected flash point is specified in many of the flash point test methods to preclude excessive losses of volatile material.

In brief, sampling for flash point determinations has three goals: (1) ensure that the isolated sample is representative of the bulk material; (2) preserve the integrity of the isolated sample; and (3) avoid or at least minimize the loss of volatile components from the material being sampled.

TABLE 5.1—Summary of Specified Sample Precooling

STM	Apparatus	Specified Sample Precooling
D56	Tag CC	27°C (80°F) or at least 10°C (18°F) below EFP
D92	Cleveland OC	At least 56°C (100°F) below EFP
D93	Pensky-Martens CC	At least 18°C (32°F) below EFP
D1310	Tag OC	At least 10°C (18°F) below EFP
D3143	Tag OC	At least 11°C (20°F) below EFP
D3278	Setaflash CC	At least 20°F (10°C) below EFP
D3828	Small Scale CC	At least 10°C (18°F) below EFP
D3941	Closed Cup	At least 20°F (10°C) below EFP
D6450	CCCFP	At least 18°C below EFP
ISO 13736	Abel CC	Below −35°C or at least 17°C below EFP[a]
IS0 3679	Closed Cup	At least 10°C below test point

[a] Whichever is higher.

CC=closed cup; OC=open cup; EFP=expected flash point

REFERENCES

[1] ASTM D4057, "Practice for Manual Sampling of Petroleum and Petroleum Products," *Annual Book of ASTM Standards*, ASTM International, West Conshohocken, PA.

[2] ASTM D4177, "Practice for Automatic Sampling of Petroleum and Petroleum Products," *Annual Book of ASTM Standards*, ASTM International, West Conshohocken, PA.

[3] ASTM D5842, "Practice for Sampling and Handling of Fuels for Volatility Measurement," *Annual Book of ASTM Standards*, ASTM International, West Conshohocken, PA.

[4] ASTM D5854, "Practice for Mixing and Handling of Liquid Samples of Petroleum and Petroleum Products," *Annual Book of ASTM Standards*, ASTM International, West Conshohocken, PA.

[5] American Petroleum Institute, *API Manual of Petroleum Measurement Standards*.

[6] ASTM D93, "Standard Test Method for Flash-Point by Pensky-Martens Closed-Cup Tester," *Annual Book of ASTM Standards*, ASTM International, West Conshohocken, PA.

[7] ISO 3679, "Determination of Flash Point–Rapid Equilibrium Closed Cup Method," International Organization for Standardization, Geneva, Switzerland, 1983.

[8] Code of Federal Regulations, Title 49, Section 173.

[9] ASTM D6450, "Standard Test Method for Flash Point by Continuously Closed Cup (CCCFP) Tester," *Annual Book of ASTM Standards*, ASTM International, West Conshohocken, PA.

[10] ASTM D56, "Standard Test Method for Flash Point by Tag Closed Tester," *Annual Book of ASTM Standards*, ASTM International, West Conshohocken, PA.

[11] ASTM D92, "Standard Test Method for Flash and Fire Points by Cleveland Open Cup Tester," *Annual Book of ASTM Standards*, ASTM International, West Conshohocken, PA.

[12] ASTM D1310, "Standard Test Method for Flash Point and Fire Point by Tag Open-Cup Apparatus," *Annual Book of ASTM Standards*, ASTM International, West Conshohocken, PA.

[13] ASTM D3143, "Standard Test Method for Flash Point of Cutback Asphalt with Tag Open-Cup Apparatus," *Annual Book of ASTM Standards*, ASTM International, West Conshohocken, PA.

[14] ASTM D3278, "Standard Test Method for Flash Point of Liquids by Setaflash Closed-Cup Apparatus," *Annual Book of ASTM Standards*, ASTM International, West Conshohocken, PA.

[15] ASTM D3828, "Standard Test Method for Flash Point by Small Scale Closed Tester," *Annual Book of ASTM Standards*, ASTM International, West Conshohocken, PA.

[16] ASTM D3941, "Standard Test Method for Flash Point by the Equilibrium Method with a Closed-Cup Apparatus," *Annual Book of ASTM Standards*, ASTM International, West Conshohocken, PA.

[17] ISO 13736, "Petroleum Products–Determination of Flash Point–Abel Closed Cup Method, International Organization for Standardization," Geneva, Switzerland, 1994.

[18] ISO 3679, "Determination of Flash Point–Rapid Equilibrium Closed Cup Method," International Organization for Standardization Geneva, Switzerland, 2003.

6

Getting Ready and Staying Ready: Preparation, Verification, and Maintenance of Apparatus

INTRODUCTION

You have received a sample or, perhaps, more than one sample, and you have been asked to determine the flash points of those samples. However, there are a number of flash point testers and methods. So, which one should you use? The question is an easy one to answer. Use the method required by the specification for the product or by the applicable regulation!

In the chapter on significance and use, we noted that many government agencies have an interest in the shipment and storage of a potentially hazardous material and have issued regulations requiring products to meet certain flash point requirements. Those regulations all specify the flash point method or methods that must be used and, where multiple methods are permitted, they will usually specify the one method that must be used in referee actions. A referee action may be required when two parties (buyer and seller, or user and government agency, for example) do not agree on the test value for the product. In those cases, a sample is sent to an independent laboratory for an unbiased determination. Specifications, like regulations, will also specify the test method or methods that are suitable for the flash point determination. (These will usually be the same as in pertinent regulations.) Also, in national and international transport regulations, when the flash point as determined by a nonequilibrium method (such as the Pensky-Martens) is within 2°C of a value at which the classification changes, an equilibrium method must be used as a referee.

In most cases, the necessary equipment will be available in the laboratory, especially if the laboratory is a quality control (QC) laboratory for the manufacturer or user of the product. However, in some cases as when a tester has worn out and has had to be replaced or when a research or commercial laboratory is entering a new field of activity, the apparatus will be sitting in its box from the manufacturer. Several questions then arise. First, where should I install the tester and what do I have to do to assemble the pieces? Second, once I've put the apparatus together, how do I assure myself that it gives the correct results? Third, what do I have to do to get it ready for the sample? Fourth, how do I maintain the apparatus in good working condition? It is those types of questions that will be addressed in this chapter.

INSTALLATION

The various test methods specify placing the apparatus on a level, steady surface (such as a table or laboratory bench) in a draft-free room. It is advisable to keep the apparatus out of direct sunlight to help keep the apparatus cool and to preclude interference with the visual detection of the flash point. In some designs, the apparatus is protected on three sides by a recommended draft shield of a suggested size. Especially for testers where the sample cup is opened for the introduction of the ignition source, it is important that the tester be in a draft-free environment. A draft can cause a decrease in the concentration of the volatile components of the sample during the test, thus giving an incorrectly high flash point result. (This may not be as critical a factor if a continuously closed-cup apparatus is being used.)

Several of the standard test methods state that tests are not to be conducted in a laboratory draft hood or near ventilators. However, ASTM Test Method D93 for the Pensky-Martens tester recognizes that some product vapors or products of pyrolysis can be objectionable [1]. Therefore, it permits placing the apparatus along with a draft shield in a ventilation hood if the draft in the hood is adjustable. The vapors can then be withdrawn without causing air currents over the test cup during the period when the ignition source is being applied. ASTM Test Method D1310 for the Tag open-cup tester recommends a location free of perceptible draft where the room temperature is maintained at 75° ± 5°F (24° ± 3°C) and in a dim light [2]. It permits tests on materials that emit objectionable vapors or products of pyrolysis to be conducted in a fume hood with the ventilation turned off. (The ventilation can then be turned on at the completion of the test or when and if the fumes become objectionable.)

All apparatus should be unpacked and assembled in accordance with the manufacturer's instructions. This is particularly important when assembling automated apparatus where designs are more likely to differ from manufacturer to manufacturer.

Among other things, actions such as the following will be required:

- Connecting the ignition source to the natural gas supply or gas cylinder where gas igniters are used, or to an electrical outlet of proper voltage and alternating current frequency where a hot-wire or spark igniter is used.
- Providing gas connections to gas burners (for manual instruments) or an electrical supply of proper voltage and frequency (for electrical heaters), for heating the test specimen in the sample cup.
- Selecting and installing the proper thermometer (for manual instrument), and using heat-transfer paste when specified by the instrument manufacturer.
- Setting the correct parameters as specified by the test method or the manufacturer.

- Ensuring that the gas cylinder is well secured when a gas cylinder is being used for either the ignition source or for heating the sample.
- Adjusting the pressure regulator on the gas cylinder to the specified pressure.
- Filling the bath with water, water-glycol, or other liquid as specified in the test method where liquid baths are used to provide heat to the sample cup.
- Adjusting the ignition source so that it follows the trajectory and reaches a point in the sample cup prescribed by the test method.

CALIBRATION AND STANDARDIZATION

The older, manually operated flash point testers are designed for the use of mercury-in-glass thermometers of standard design such as the ASTM or IP (Institute of Petroleum, now called Energy Institute) thermometers. However, where non-standard thermometers or alternative temperature-sensing devices are provided, calibration against standards traceable to the national standard may be required.

The small-scale closed tester described in ASTM Test Method D3828 uses electrical heating to control the temperature of the metal block in which the sample cup is heated [3]. In early models, the level of heat was controlled by a dial or sometimes two dials (one for coarse and the other for fine control) and required plotting the relationship between the temperature dial settings and the readings on the thermometer that was inserted, along with heat transfer paste, into a hole in the heating block. In modern small-scale testers, this procedure has been replaced by digital temperature selection and control plus automatic flash detection. The platinum-resistance thermometer that is now used is a robust and stable device and seldom requires calibration.

In some of the modern small-scale testers, a barometer is integrated into the system. Although this barometer is calibrated for pressure and temperature during manufacture, it should be verified by the user and recalibrated if necessary.

The continuously closed-cup (CCCFP) tester described in ASTM Test Method D6450 and ASTM Test Method D7094 (MCCCFP) use a pressure increase as an indication that a flash has occurred [4,5]. It is necessary to check the calibration of the pressure transducer used to sense this pressure increase, both when the apparatus is initially assembled and when QC checks performed in accordance with the test method indicate the need. The ambient atmospheric pressure is used as the reference point, so it is necessary that the ambient pressure displayed by the apparatus and the ambient barometer pressure be the same. If not, the control knob for the transducer is adjusted until the readings are the same. It has been noted earlier that the barometer used should not be one of those precorrected to sea level but, rather, should indicate the actual atmospheric pressure at the location of the tester.

In automated flash point instruments, the sensor for the sample temperature is generally a Pt-100 or a nickel-chromium/nickel or similar thermocouple. Such temperature sensors are generally calibrated by the manufacturer before shipment so, on setting up the apparatus, it is only necessary to verify that the temperature-measuring system is still reading correctly. A full calibration is not needed unless the temperature reading is found to be incorrect when the verification check is made or when indicated by QC checks during the routine use of the instrument. When a thermocouple must be calibrated, it is essential that the person doing the calibration use only reference thermometers that are traceable to the National Institute of Standards and Technology (NIST, the former Bureau of Standards), or to national authorities in the country in which the apparatus is being used.

VERIFICATION AND QC

Verification

Having assembled a flash point tester and having calibrated and standardized as specified in the test method or by the manufacturer, an operator is bound to want some confirmation that the tester will now produce accurate results. For that purpose, the operator needs to obtain and run a certified reference material (CRM) on first assembly and periodically thereafter.

For flash point testing, a CRM is a high purity (99 + mol percent purity) hydrocarbon or other stable petroleum product with a method specific flash point established by a method-specific interlaboratory study following ASTM Practice D6300 or ISO Guides 34 and 35 for the statistical evaluation of the results [6–8]. Some CRM samples are a fuel or a lubricant more like the material usually tested. CRMs can be obtained from some national standardization bodies and from some calibration standard suppliers. Certificates of performance including an uncertainty figure for the specific test method should be provided with such materials because the flash point value is dependent upon the composition of each CRM batch and upon the test method used. Sometimes such CRM samples can be certified for tests other than flash point.

Prior to 1994, *p*-xylene was the verification fluid cited for most flash point test methods. However, *p*-xylene suffered from two deficiencies. First, it was toxic. Second, its flash point of about 27°C (81°F) was lower than the range of flash points normally determined. Therefore, ASTM Committee S-15, the Coordinating Committee on Flash Point, provided funds to NIST to procure quantities of *n*-decane, *n*-undecane, *n*-tetradecane, and *n*-hexadecane. These materials were then sent out to a number of laboratories to determine their flash points by ASTM Test Methods D56 (Tag closed cup), D92 (Cleveland open cup), D93 (Pensky-Martens closed cup), D3278 and D3828 (small-scale closed cup) [3,9–11]. After providing the four materials for several years, NIST decided to discontinue supplying these verification fluids. Several commercial organizations now provide these four materials in 250-mL and other size units. Other reference materials are sometimes cited as shown in Table 6.1.

Table 6.1 is a compilation of CRMs listed in a number of ASTM flash point standards. The standard is shown together with the CRM and the flash point. One fact becomes obvious from an examination of the table, specifically, that the flash point is method specific. For example, for *n*-decane, flash points of 50.9°, 52.8°, and 49.7°C are cited in ASTM Test Methods D56 (Tag closed cup), D93 (Pensky-Martens closed cup), and D3828 (small-scale closed cup), respectively. For *n*-undecane, values of 67.2°, 68.7°, and 65.9°C are cited for the same three test methods. Only two ASTM standards cite *n*-tetradecane and *n*-hexadecane. The flash points of *n*-tetradecane are given as 115.5° and 109.3°C, and the flash points of *n*-hexadecane are given as 138.8° and 133.9°C in ASTM Test Methods D92 (Cleveland open cup) and D93 (Pensky-Martens closed cup), respectively. Flash points obtained by open cup methods are generally higher than those obtained by closed-cup methods.

Table 6.2 shows CRMs and their approximate flash points listed in ISO Method 3679 and, for two of the CRMs, shows the flash point values cited in ASTM Test Method D3828 [3,12]. (Both ISO 3679 and ASTM Test Method D3828 use the small-scale tester originally known as the Setaflash tester.) ISO Method 3679 (1983) cites nominal flash points of 49° and 63°C for *n*-decane and *n*-undecane, respectively, whereas ASTM Test Method D3828 cites 49.7° and 65.9°C for the same two compounds.

Assume that you have obtained a CRM with a certificate indicating its flash point for the method you are using (corrected to the standard barometric pressure, of course). Assume further that you have run a test with the CRM in your instrument. It is highly likely that the value for the corrected flash that you obtain will differ from the certificate value. How much difference can be accepted as normal experimental variation? ASTM Test Method D56 states that the limits of variation "can be determined from the reproducibility value of the test method, reduced by interlaboratory effect and then multiplied by 0.7," whereas ISO 3679 states that for a single test made on a CRM or SWS (secondary working standard; see next section), the difference between a single result and the certified value of the CRM or the assigned value of the SWS should be less than or equal to the reproducibility of the test method divided by "the square root of 2." The limits for the batches of CRM cited in the ASTM test methods range from 0.8° to 8°C, but it is necessary to use the value cited for the particular batch of CRM used in verifying the instrument.

ASTM Practice D6299 provides guidance on the application of quality assurance techniques to the evaluation of analytical measurement system performance [13]. This standard was written for use with petroleum products and lubricants, but the principles are generally applicable. First, the standard refers to a "check standard" that is defined as a material having an accepted reference value used to determine the accuracy of a measurement system. A check standard is preferably a material that is either a certified reference material traceable to a nationally recognized body or a material that has an accepted reference value established through interlaboratory testing. (Note: This type of check standard of Practice D6299 is what has been called a CRM in the flash point standards.)

TABLE 6.1—CRM Flash Points (°C) Cited in Some ASTM Test Methods

CRM Compound	D56 TagC	D92 Clev.	D93 P-M	D1310 TagO	D3278 Sml-Sc	D3828 Sml-Sc	D6450 CCCFP	
n-Heptane				−5				
p-Xylene				33	27.2			
n-Butanol					36.7			
Anisole								43.9
n-Decane	50.9		52.8			49.7		
n-Undecane	67.1		68.7			65.9		
n-Dodecane							79	
n-Tetradecane		115.5	109.3					
n-Hexadecane		138.8	133.9					
Diethylene glycol				146				

TABLE 6.2—CRM Flash Points (°C) in ISO 3679 and Comparison with ASTM Test Method D3828

CRM Compound	ISO 3679	ASTM D3828
2,2,4-Trimethyl pentane	−9.5	No Value
Methyl benzene (toluene)	+6.0	" "
n-Octane	11	" "
1,4-Dimethylbenzene	27	" "
n-Nonane	32	" "
n-Decane	49	49.7
n-Undecane	63	65.9
n-Dodecane	81	No Value
n-Tetradecane	129	" "
n-Hexadecane	134	" "

Practice D6299 also states that check samples can be prepared from a material that is analyzed under reproducibility conditions using multiple measurement systems. The accepted reference value (ARV) for such check samples is then the average after statistical examination and outlier treatment has been applied. Because the uncertainty in the ARV is inversely proportional to the square root of the number of values in the average, Practice D6299 recommends the minimum of 16 nonoutlier results be used in calculating the ARV.

QC

Practice D6299 cites five primary activities that can be undertaken in a quality assurance program. Monitoring accuracy has been addressed above. A second activity is proficiency testing through participation in interlaboratory exchange programs where such programs are available. There are a number of ASTM crosscheck programs where petroleum product specification tests including flash point are run. Laboratory management may find it advantageous to participate in one or more of those programs, or in crosscheck programs run by other organizations. For example, in Germany, both the Deutsches Institut für Normung and the Fachausschuss Mineralol und Brennstoffnormung conduct an annual round robin for a large number of methods including flash point. Participation in such crosscheck programs enables a laboratory to compare its results against those obtained by a number of other laboratories.

A third activity listed by Practice D6299 is monitoring stability and precision through QC testing. Such QC testing should be conducted at the beginning of any set of measurements and immediately after a change is made in the measurement system. The QC samples should be handled in the same manner and under the same conditions as samples that are routinely analyzed. Special treatment of the QC samples should be avoided as this undermines the integrity of resulting precision estimates. Check standards (CRMs) may be used as QC samples, but normally the cost of such samples precludes their use. Instead, special QC samples are prepared from the type of material being analyzed. Such samples are called SWS in the flash point test methods.

SWS are stable, homogeneous material available in the quantity needed for the QC program. These are usually inhouse materials that are representative of the typical sample being tested, for which the mean flash point and the statistical control limits (±3 sigma or three standard deviations) have been established using standard statistical techniques. Practice D6299 instructs us to collect the material in a single container, to mix the material thoroughly to ensure homogeneity, and to conduct any testing necessary to ensure that the sample meets the characteristics for its intended use. If necessary, this bulk material is then split into separate, smaller containers to insure integrity over time. For example, samples containing volatile matter (a common occurrence when flash points are to be determined) could lose volatile matter if a single container were opened repeatedly to obtain subsamples for testing. Also, samples prone to oxidative deterioration may have to be blanketed with an inert gas prior to the subsamples being sealed. It is suggested that a new batch of SWS be prepared when the amount remaining from the previous batch can support no more than 20 QC tests.

The data obtained when SWS samples are tested are screened, statistical techniques are used to identify erroneous data, and control charts are prepared. Results are analyzed to quantify the bias and precision estimates for the measurement system. The assessment is conducted only after at least 15 results have become available. First, the data are screened for data that are inconsistent with the remainder of the data set, such as may occur if numbers are transposed in transferring the result. If, after discarding suspicious results for cause, there are fewer than 15 values remaining, additional data must be collected. The data are also screened for unusual patterns such as nonrandom patterns on a run chart. Such unusual patterns are cause for discarding the data and start over again. Another test is for normal probability distribution. Details regarding the above screening and on the preparation of control charts may be found in Practice D6299.

Deviations from Accepted Reference Value[1]

Assume that you have run a CRM or an SWS in your flash point apparatus and the value for the flash point obtained falls outside the indicated limits of the accepted reference value. What should you do and what should you not do? The second part of the question is the easier to answer–do not start calibrating the temperature-measuring system! The temperature-measuring systems are seldom at fault. What should be done is to follow a logical check list of possible causes. Remember, there are three sources of measurement error: the sample, the operator, and the instrument.

First of all, check the age of the CRM or SWS. A CRM has a shelf life of less than 1 year, but once a CRM has been opened, the certified value is questionable as losses of volatile components from an open container may occur. Hence, if an unopened CRM has been in the lab's possession for more than 1 year, it should probably be discarded. If an opened CRM has been used, it may be a good idea to recheck using a new CRM. If an SWS has been stored in bulk rather than in subdivided units adequate for one determination, and if it has been in use for a period of time, the gradual loss of volatile components may have caused a drift away from the originally determined value, so check the available data to see whether the differences between the original value and the value obtained in the check tests have been growing greater. If so, it may be a good idea to check again using a new CRM or SWS.

If the sample has been eliminated as the source of the difference between the ARV and the measured value, then consider the possibility of errors in procedure have crept into the operator's test techniques and explore the details of the procedure actually practiced. Such errors have been known to occur. This is particularly important where manual methods have been used as much more of the test process is under the operator's control, whereas with automated instruments much more of the process is out of the operator's immediate control. Check such details as the manner in which the sample was transferred to the test cup, the speed at which the temperature of the sample was increased, and the intervals at which the ignition source was applied. Another possibility is that the wrong test method has been

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[1] Based upon information provided by R. G. Montemayor, K. Shimodaira, and others.

used, e.g., that a CRM for a Pensky-Martens test procedure has been used to check a Cleveland open-cup procedure. Finally, because the determined flash points are corrected for the barometric pressure, verify that the barometric pressure–measuring device has been installed, calibrated, and used in the proper manner. A barometric pressure reading that is higher than actual will result in a lower than actual flash point temperature being indicated, and vice versa.

Having eliminated sample deterioration and operator error as causes of the excessive deviation of the determined value from the ARV, we must finally turn to the instrument as the cause. Check the easy factors first. Is the sample cup (and, with closed-cup methods, the sample cup lid) clean and free of accumulated deposits or of residual cleaning solvent? Is there a draft around the instrument (particularly important with open-cup methods)? Does the ignition source follow the prescribed path and reach the proper position in the sample cup? Is the size of the ignition flame correct? In the case of electrical igniters, is the igniter current properly adjusted? In automated instruments, is the flash-sensing system, e.g., ionization rings, clean and properly positioned? Correct anything found to be incorrect. If nothing on such a checklist as indicated above is found out of order, then and only then should the temperature-measuring system be verified.

Tables 6.3 and 6.4 are checklists of potential problems and suggested actions. The former shows potential problems that lead to higher than actual flash points; the latter shows potential problems that lead to lower than actual flash points.

PREVENTIVE MAINTENANCE FOR FLASH POINT EQUIPMENT[2]

The maintenance of flash point equipment should not be dependent upon getting an alarming result from a CRM check sample or from an SWS QC sample. Operators should get in the habit of conducting a quick visual check whenever they are about to run a flash point determination, and a more thorough check should be conducted at intervals dependent upon the frequency of use of the instrument, at least annually and more frequently for instruments in constant use.

There are many parts of a flash point apparatus that can deteriorate and cause an inaccurate flash point temperature

TABLE 6.3—Potential Problems Causing Higher Than Actual Flash Points

Potential Problem	Suggested Action
Dirty test cup	Clean test cup
Dirty test cup lid	Clean test cup lid
Lid too loose	Use cover with proper fit
Test flame too small	Adjust to proper flame size
Igniter current too low	Adjust igniter current
Shutter assembly sticking	Lubricate assembly[a]
Application time of ignition too short	Correct application time
Heating rate too slow	Adjust to correct rate
Stirring rate too slow	Adjust to correct rpm
Temperature reading too high	Check and correct thermometer
Flash detection device not seated right	Correct seating
Barometric pressure reading low	Check; correct barometer

[a] Use proper high-temperature lubricant.

TABLE 6.4—Potential Problems Causing Lower Than Actual Flash Points

Potential Problem	Suggested Action
Test flame too big	Adjust to proper flame size
Igniter current too high	Adjust to proper current
Ignition source application too long	Correct application time
Heating rate too high	Adjust to proper rate
Stirring rate too high	Correct the stirring rpm
Barometric pressure reading high	Check; correct barometer

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[2] Much of this section is based upon notes provided by R. G. Montemayor, Volkmar Wierzbicki, and Roland Aschauer.

to be indicated. Many of these have been mentioned above in the checklists for causes of high and of low flash point results. Every time a flash point determination is made, the operator should check that the sample cup and the lid (for the closed-cup apparatus) are clean. If the previous sample has not been completely removed from the cup, a high or a low flash point may be obtained depending upon the nature of the previous sample. Also, if the solvent used for cleaning these parts of the apparatus has not been completely evaporated, the solvent could cause a low flash point value. If the solvent has not been fully effective, a deposit could have been left that would reduce the rate of heat transfer through the test cup and result in an artificially high flash point.

Another aspect the operator should check on manual equipment is the size of the ignition source flame. Some apparatus has a bead or other indicators on the apparatus to show the proper size of the flame.

Part of the periodic maintenance check must be to check the path of the ignition source for adherence to the test method specification. The ignition source path and its closest approach to the surface of the test fluid are specified in the test methods. If the mechanism by which the ignition source is introduced (to check whether the flash point has been reached) has suffered from wear and tear, the ignition source may approach closer to the fluid surface than specified or, alternatively, may fail to reach the specified closeness. The former situation could lead to low flash point indications and the latter to high flash point indications.

If the ignition source is a hot-wire type, the temperature of the glowing wire should be over 1200°C as temperatures below that affect the result. This temperature is a function of the electrical current passing through the element. During periodic maintenance checks, the current should be checked for conformance to the manufacturer's specification. The shape of the igniter, which may be bent easily, should also be checked to see that it conforms to the manufacturer's specification. Further, the periodic check should include inspections for damaged seals, shutters that are not light tight, stirrers that rotate at incorrect speeds, and automated temperature controls that fail to provide the correct rate of temperature increase.

A maintenance check must also include a verification of the temperature-measuring system. In the midst of a busy day in the laboratory, a nonstandard or uncalibrated thermometer may have been used to replace one inadvertently broken. Therefore, the periodic maintenance check of manual equipment should ascertain that only thermometers that meet the requirements of the test method have been used.

Automated flash point testers are much more complicated than the simple manual apparatus. Because designs differ from manufacturer to manufacturer and from one type of tester to another, e.g., from Cleveland open cup to Pensky-Martens closed cup, the recommendations of the individual manufacturer should be followed. The following shows some typical checks that will be specified:

- Check of all electrical cords and gas hoses for abrasions, bare wires, or leaking hoses. Check the main switch, the cord, and the plug. Check the fuses to see that they are the sizes specified by the manufacturer.
- Check for loose elements and tighten or replace as necessary. Lubricate with suitable high-temperature grease. Be certain the proper lubricant is used and used only on specified parts, as contamination with lubricant can cause a false flash point. Check that cup and lid are clean, and that the lid opening for the ignition source opens and closes fully.
- Where applicable, inspect the electro-ignition system, which ignites the test flame, to be certain the glow wires have not been compressed or knocked out of alignment.
- Check the flash detection sensor for broken thermocouple wires or glass covering. Check for any deposits that could interfere with detection.
- Check that the gas flow to the ignition flame is not obstructed and clean the hose if necessary. Check that the ignition flame is the correct size.
- Check that the stirrer is operating correctly. Be careful that lubricant from the stirrer bearing does not contaminate the system.
- Check that the heating rate is that specified for the test method.

All of these may not be needed with some testers, e.g., testing of lids would not be needed on open-cup models.

Some daily maintenance may also be required. Again, follow the recommendations of the manufacturer in addition to any instructions for preparing a tester in the test method. As an example, the manufacturer of the CCCFP apparatus advises that the surface of the oven plate should be cleaned with solvent and tissue daily, taking care not to scratch the surface. They also advise cleaning the arc pins to ensure easy ignition (the tester uses a spark-ignition system).

SUMMARY

In this chapter, we have discussed the steps necessary to put a new flash point tester into use and how to keep it operating properly. The apparatus must be assembled and adjusted in accordance with the test method and the manufacturer's instructions, and various calibrations and verifications must be performed. Then the instrument must be checked using a certified reference material (verification fluid). During use, a secondary working substance may be used for periodic checking but, at least once a year for a tester in daily use, the tester should be checked against a CRM. Some daily plus periodic maintenance may be required, and more extensive maintenance may be required if verification tests are unsatisfactory.

REFERENCES

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[3] ASTM D3828, "Standard Test Method for Flash Point by Small Scale Closed Tester," *ASTM Book of Standards,* ASTM International, West Conshohocken, PA.

[4] ASTM D6450, "Standard Test Method for Flash Point by Continuously Closed Cup (CCCFP) Tester," *ASTM Book of Standards,* ASTM International, West Conshohocken, PA.

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[8] ISO Guide 35, "Certification of Reference Materials–General and Statistical Principles."

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7

Procedures, Corrections, and Reporting

INTRODUCTION AND OVERVIEW

The sample is waiting. The flash point instrument has been assembled and verified, and a qualified operator is available. It is now time to conduct the specified flash point test and to report the results. In this chapter, the various test procedures, the correction of the raw data, and the reporting of the final results will be discussed. However, because the procedures are provided in infinite detail in each of the various test methods, they will not be repeated here. Rather, we will examine the general principles on which those procedures are based and the similarities and differences among the various test methods. We will also examine the correction of the raw data to a common sea level pressure of 101.3 kPa (760 mmHg). Finally, we will discuss some of the information that should be included in the report of results.

TEST PROCEDURES FOR FLASH POINT

There are a large number of standard methods for flash point determinations. We will be referring to eleven ASTM test methods and to three ISO methods, but there are numerous other flash point methods that have been standardized by various national standardization bodies and organizations. It should be recognized that all flash point methods are empirical. Also, these methods can be categorized in various ways: dynamic methods (where the vapors above the test specimen and the specimen are not at temperature equilibrium when the ignition source is applied); equilibrium methods (where the vapors above the test specimen and the specimen are at temperature equilibrium when the ignition source is applied); finite flash point or flash/no-flash methods; manual or automated methods; open-cup or closed-cup methods, etc.

Dynamic Manual Methods

The original flash point methods developed from the middle of the nineteenth century through the early part of the twentieth century were all manual and all dynamic methods for the determination of finite flash points. They were all essentially simulations of real-life situations, i.e., spills in open areas simulated by open-cup methods or spills in confined areas simulated by closed-cup methods. ASTM standardization of the methods started in 1918 when what is now Committee D02 on Petroleum Products and Lubricants standardized ASTM Test Method D56, which used the Tag closed-cup tester [1]. This was followed in 1921 by ASTM D92 and by ASTM Test Method D93, which used the Cleveland open-cup tester and the Pensky-Martens closed tester, respectively [2,3]. Later, in 1952, Committee D01 on Paint and Related Coatings, Materials, and Applications standardized the use of the Tag open-cup apparatus as ASTM Test Method D1310 and, in 1962, Committee D04 on Road and Paving Materials issued ASTM Test Method D3143, which adopted the Tag open-cup apparatus for determining the flash point of cutback asphalts [4,5]. Although the Abel closed-cup apparatus had been adopted as a standard in the United Kingdom during the late 19th century, it was not until December 1994 that the International Organization for Standardization (ISO), Technical Committee 28, issued a draft international standard, ISO/DIS 13736, for the Abel method [6].

Open-Cup vs. Closed-Cup Methods

The six test methods mentioned above fall into two categories: closed-cup methods and open-cup methods. ASTM Test Methods D56, D93, and ISO/DIS 13736 are closed-cup methods, whereas ASTM Test Methods D92, D1310, and D3143 are open-cup methods. However, the basic test methods are the same. A test specimen is transferred at a specified temperature below the expected flash point (EFP) to a precooled sample cup. The temperature of the test specimen is then heated using a specified rate until it reaches a specified number of degrees Celsius or Fahrenheit below the EFP. At that temperature and at specified temperature intervals thereafter, the vapors above the liquid sample are tested by the application of an ignition source, usually a flame of specified size, to ascertain whether a flash point has been reached.

Applicable Temperature Range

The procedures in some of these test methods are subdivided dependent upon flash point range or other factors. Thus, among the closed cup methods, ASTM Test Method D56 has two procedures: one for flash points below 60°C (140°F) and the other for flash points above or at that level. ASTM Test Method D93 has a Procedure A and a Procedure B with the former applied to distillate fuels and the latter to residual fuels. (A recent version of ASTM Test Method D93 includes a Procedure C that applies to biodiesel fuel. See latest ASTM Test Method D93 for details of Procedure C). ISO/DIS 13736 also has two procedures with one applying to flash points from −30°C to +18.5°C and the other applying to flash points from +19°C to +70°C. Among the open-cup methods, only ASTM Test Method D1310 has multiple procedures. One covers the flash point range from 0° to 60°F (−18° to +16°C); the second from 60° to 200° F (16° to 93°C); and the third from 200° to 325°F (93° to 165°C). Although the test procedures for the subdivisions under any one test method are similar, differences do exist in such things as the heating rate and the stirring rate, where a stirrer is used, so care must be taken to follow the prescribed procedure.

Precooling Requirement

In general, the various test methods call for cooling the main laboratory sample to a specified temperature before removing the test specimen. In some cases, the graduate, syringe, or other equipment for transferring the test specimen into the sample cup and the sample cup itself must also be precooled. In a few cases, the bath temperature must be adjusted to a specified temperature. Such cooling instructions often take the form of directions to cool to a specified temperature or to a certain number of degrees below the EFP, whichever is higher.

Ignition Flame Size

The size of the ignition flame in the six test methods is roughly the same (4 mm), although expressed in different ways. Thus, D56 calls for a flame size of 4.0 ± 0.8 mm, whereas that for the D93 test method must be 3.2 to 4.8 mm, and that for ISO/DIS 13736 is given as 3.8 mm. Among the open-cup methods, D92 specifies 3.2 to 4.8 mm, D1310 specifies 4.0 mm, and D3143 specifies the size of the bead but "no more than 4.0 mm." The apparatus in all cases usually has a bead or other indication attached to the apparatus as a guide to the size of the test flame.

Testing Cycle Time (Duration of Ignition Source Application)

To test whether a flash point temperature has been reached, the test flame is dipped into a closed cup or passed over the open sample cup following a prescribed path. The testing cycle time (length of time at which ignition source is applied to the test apparatus to test if a flash point is observed) is specified in all six of the test methods. In ASTM Test Methods D56, D92, D1310, and D3143, the testing cycle is limited to about 1 s. In ASTM Test Method D93, 1.5 s is the specified cycle time and in ISO/DIS 13736, a cycle time of about 3 s is permitted. In the closed-cup tests, the cycle time involves withdrawing the slide to open the cup, dipping in the test flame, staying briefly at the lowest part of the path, removing the flame, and closing the slide. In the open cup, the cycle time is the time required to follow the prescribed path from one side of the cup to the other (the flame moves in one direction only during any check of the flash point).

Heating Rate and Sample Stirring

The heating rate differs widely among the test methods and within a test method among the subprocedures. It can even vary during different segments of the same procedure. For the <60°C procedure in ASTM Test Method D56, the temperature is allowed to increase 1°C or 2°F every minute ± 6 s. The ≥60°C procedure of ASTM Test Method D56 allows a 3°C or a 5°F increase every minute ± 6 s. The Pensky-Martens D93 test Procedure A (for distillate fuel oils) specifies a 5° to 6°C (9° to 11°F) rise per minute, whereas Procedure B (for residual fuel oils) specifies a 1° to 1.5°C (2° to 3°F) rise per minute. (A recent version of ASTM Test Method D93 includes a Procedure C that applies to biodiesel fuel. See latest ASTM Test Method D93 for details of Procedure C). The ISO/DIS 13736 test method using the Abel apparatus specifies a 1°C per minute rise in temperature for the lower temperature procedure and also for the higher temperature procedure.

Before continuing with an examination of the temperature rise rates of the open-cup apparatus, let us note that the Pensky-Martens apparatus is equipped with a stirrer having an impeller diameter roughly 75 % of the internal diameter of the sample cup. This stirrer rotates at 90 to 120 rpm during Procedure A tests and at 250 ± 10 rpm during Procedure B tests. Stirring not only aids the distribution of heat throughout the liquid in the sample cup but also, by increasing the velocity past the sides and bottom of the cup, increases the rate of heat transfer into the cup contents. Hence the stirrer assists in providing the high rise rates specified in the two Pensky-Martens procedures. Although the Abel apparatus also has a stirrer, its impeller is only about 56 % of the diameter of the sample cup and the rotation of the stirrer is only 30 rpm. Although this assists the distribution of heat throughout the cup contents, it is not as effective in helping the transfer of heat from the surrounding bath through the cup walls.

The ASTM D92 Cleveland test method has a single procedure which specifies a 14° to 17° C (25° to 30°F) temperature increase per minute in the early part of the test but decreases this to 5° to 6°C (9° to 11°F) temperature increase per minute during the last 28°C (50°F) before the flash point temperature is reached. This high rate is obtained through the direct contact of the sample cup with a heating plate that is heated electrically or by a gas burner, thereby developing a high temperature differential between the exterior and interior of the sample cup. ASTM Test Method D1310 (the Tag open-cup method) has three procedures but all three specify a temperature increase rate of 1°C ± 0.25°C (2° F ± 0.5°F) per minute as the temperature approaches the EFP. ASTM Test Method D3143 (the Tag open-cup method for cutback asphalts) also specifies a 1°C ± 0.25°C per minute rise rate but without the Fahrenheit equivalent rise rate.

Flash Point Check Temperature and Interval

The various test procedures also differ in the temperature at which a check is made for the flash point and in the temperature intervals at which flash point checks are made thereafter. For EFP below 60°C, the ASTM Test Method D56 test method starts 5°C (or 10°F) below the EFP and checks every 0.5°C (or 1°F) until a flash is noted. With expected flash points above 60°C, the first check is made at the same number of degrees below the EFP, but the check interval is increased to 1°C (or 2°F). In ASTM Test Method D93 Procedure A (for distillate fuel oils), the first check for flash point is made 23° ± 5°C (or 41° ± 9°F) below the EFP. Then, if the EFP is below 110°C (or 230°F), a check for a flash is made every 1° C (or 2°F) or, if the EFP is above 110° C, a check is made every 2°C (or 5°F) after the initial check. In ASTM Test Method D93 Procedure B (for residual fuel oils), the same number of degrees below the EFP and the same check intervals are specified. In the ISO procedure using the Abel apparatus, the first check is made 9°C below the EFP and checks are made every 0.5°C thereafter until a flash is noted.

An examination of the open-cup methods shows that ASTM Test Method D92 using the Cleveland open-cup apparatus calls for the first check is to be made at 28°C below the EFP and subsequent checks are to be made every 2°C thereafter until a flash is noted. The ASTM Test Method D1310 procedure (and the ASTM Test Method D3143 procedure, which is similar) calls for raising the liquid test specimen to 20°F (or 10°C) below the EFP, which is determined by a preliminary test. Then, checks for flash point are made "at two intervals of 5°F (3°C) and then at intervals of 2°F (1°C) until the flash point is reached."

The above information on heating rates, ignition cycle times, and flash point check intervals are summarized in Table 7.1 for the closed-cup methods and in Table 7.2 for the

TABLE 7.1—Heating Rates and Check Intervals for Closed-Cup Manual Methods

Test Method & F.Pt. Range	Heating Rate °C/min	Ignition Cycle, Sec	Start Check °C <EFP	Check Interval °C
D56 Tag				
< 60°C	1	1	5	0.5
60° to 93°C	3	1	5	1.0
D93 Pensky-Martens				
Proc.A < 110°C	5–6	1.5	23 ± 5	1
> 110°C	5–6	1.5	23 ± 5	2
Proc.B < 110°C	1–1.6	1.5	23 ± 5	1
> 110°C	1–1.6	1.5	23 ± 5	2
DIS 13736 Abel				
−30° to +18.5°C	1	~ 3	9	0.5
+19 to +70°C	1	~ 3	9	0.5

Cleveland and Tag open-cup methods. Because special situations exist in the various methods, these tables should be considered only guides for comparison purposes and are not substitutes for the information in the test methods. Only the Celsius values given in the test methods are shown, to keep a consistent set of units. Test method ASTM Test Method D3143 defers to ASTM Test Method D1310, so the two methods are combined in Table 7.2 rather than duplicate values. Note that these two Tag open-cup methods specify two checks at 3°C intervals, followed by 1°C intervals thereafter until a flash is noted.

This completes the discussion of the basic procedures used in the old manual closed- and open-cup methods. However, before discussing the automated versions of some of these methods, there are several special situations that are mentioned in some of the test methods, specifically, masking phenomena, film formation, and hydrolysis. The first and last are mentioned in closed-cup methods, the second in open-cup methods.

Flash Point Masking Phenomenon

Flash point masking is a phenomenon mentioned in closed-cup ASTM Test Methods D56, D93, E502 as being associated with mixtures containing halogenated hydrocarbons such as methylene chloride and trichloroethylene [7]. (ASTM Test Method E502 is a standard test method of ASTM Committee E27 on Hazard Potential of Chemicals, which adapts various dynamic and equilibrium closed-cup methods to the determination of flash point of chemicals.) With liquid materials containing such halogenated hydrocarbons, no distinct flash is noted, but there is a significant enlargement (not a halo) of the test flame and a change in its color from blue to yellowish-orange. Heating above ambient temperature can result in significant burning of vapors outside the test cup, which can result in a potential fire hazard. ASTM Test Methods D56 and D93 recommend that testing be discontinued, if such conditions are encountered during testing. The two methods also note that, when a liquid contains both flammable and nonflammable components, the mixture may not exhibit a closed-cup flash point because the nonflammable components are sufficiently volatile and present in sufficient quantity to inert the vapor space in the closed cup. ASTM Test Method E502 points out that such mixtures may exhibit an open-cup flash point and, further, that the spillage of such materials may lead to the evaporation of the nonflammable components leaving a flammable residue.

The flammability of a substance can also be masked by the size of the flash point cup. For example, some substances such as trichloroethylene requires a large diameter for

TABLE 7.2—Heating Rates and Check Intervals for Open-Cup Manual Methods

Test Method F.Pt. Range	Heating Rate °C/min	Ignition Cycle, Sec	Start Check °C < EFP	Check Interval °C
D92 Cleveland				
79° to 400°C	5–6	1 ± 0.1	28	2
D1310/D3143 Tag				
−18° to + 16°C	1 ± 0.25	1	15	3 (2), then 1
+16° to + 93°C	1 ± 0.25	1	15	3 (2), then 1
+93° to +165°C	1 ± 0.25	1	15	3 (2), then 1

flash propagation, so it exhibits no flash in a flash point tester but will burn when ignited in apparatus of sufficient size.

ASTM Test Method E502 also mentions that, in some instances, an open-cup flash point tester will yield a lower flash point than a closed-cup tester, a situation the reverse of that normally experienced. Such phenomena are associated with materials that hydrolyze with the moisture in the air to form flammable by-products.

Surface Film Formation during Flash Point Testing

ASTM Test Methods D92, D1310, and D3143 mention that some substances produce surface films that inhibit the passage of volatile material into the vapor space above the test cup and leads to higher flash points. Several means are suggested to overcome this problem. ASTM Test Method D92 suggests that, prior to each application of the ignition source, such films be moved to one side, e.g., with a spatula. Both ASTM Test Methods D1310 and D3143 suggest that a stirring rod be inserted about 15 s before the ignition source is passed over the open cup, and moved three or four times along the approximate path followed by the ignition source. ASTM Test Method D1310 suggests the rod be inserted about $^1/_2$ in. (15 mm) and ASTM Test Method D3143 suggests a 13-mm insertion. Regardless of whether the spatula method or the rod method is used, the essence is to free a portion of the surface of any film inhibiting the movement of volatile matter into the vapor space. ASTM Test Method D92 appends an alternative method involving the insertion of a filter paper into the base of the Cleveland sample cup. (For details, see Appendix X1 of ASTM Test Method D92.)

Automated Versions of Dynamic Manual Testers

Automated versions of the dynamic methods using the Tag closed-cup, the Cleveland open-cup, the Pensky-Martens closed-cup, and the Abel closed-cup apparatus are mentioned in ASTM Test Methods D56, D92, D93, and ISO/DIS 13736, respectively. In general, the basic manual procedures, including the heating rate control, are conducted automatically once the test specimen has been transferred to the sample cup. Either a gas flame or an electric igniter (spark or hot wire) are usually permitted. A flash is, however, identified by means other than the human eye, as was noted in the earlier discussion of apparatus. Many of the methods defer to the manufacturer's instructions for assembly and care of the apparatus.

All specify that the sample cup shall conform to the dimensions of the manual sample cup. In addition, the Pensky-Martens test method (ASTM Test Method D93) specifies that "the apparatus shall use the test cup, test cover and shutter, and ignition source device described . . . in Annex A1." (Either a flame or an electrical igniter of the hot-wire type is permitted.)

The ISO/DIS 13736 standard for the Abel apparatus states that equipment that is partially or wholly automated may be used, if it has been established that the results obtained will not differ from those obtained with the manual procedure. Further, the standard instructs that all of the manufacturer's instructions for calibrating, adjusting, and operating should be followed and also specifies that, if there is a disputed result, the flash point determined manually shall be the referee test.

Finite Equilibrium Flash Point Methods

In determining finite equilibrium flash points, the sample cup and its contents must be allowed to approach temperature equilibrium by holding for a period of time at the test temperature or by use of a slower heating rate than that in the dynamic methods noted earlier where a flash check is made as the test specimen reaches the test temperature.

The small-scale, closed-cup tester is used in a number of standard tests. Some of these standards incorporate both finite flash point determinations and flash/no-flash tests, but only the finite flash point methods will be discussed at this point. ASTM Test Method D3278 [8], first published in 1973, summarizes the basic procedure as follows:

"For a finite flash point measurement, the temperature is sequentially increased through the anticipated range, the test flame being applied at 5°C (9°F) intervals until a flash is observed. A true determination is then made, using a fresh specimen, starting the test at the temperature of the last interval before the flash point of the material and making tests at increasing 0.5°C (1°F) intervals."

ASTM Test Method D3828 [9], first published in 1979, uses a somewhat different procedure, which is summarized as follows:

"A specimen of a sample is introduced into the cup of the selected apparatus that is maintained at the expected flash point. After a specified time, a test flame is applied and an observation made as to whether a flash occurred.

"The specimen is removed from the cup, the cup cleaned, and the cup temperature adjusted 5°C (9°F) lower or higher depending on whether or not a flash occurred previously. A fresh specimen is introduced and tested. This process is repeated until the flash point is established within 5°C (9°F). The procedure is then repeated at 1°C (2°F) intervals until the flash point is determined to the nearest 1°C (2°F)."

ISO 3679 states the principle of the method as follows:

"A test portion of specified volume is introduced into the test cup, which is maintained at the temperature of the estimated flash point of the material under test. After a specified time, a test flame is applied and the presence or absence of flash observed. Further tests, with fresh portions at different temperatures, are carried out until the flash point is determined to the sensitivity specified" [10].

Various models of the small-scale closed-cup apparatus are available. ASTM Test Method D3278 specifies a model where the 2-mL test specimen is injected into the sample cup using a syringe. ASTM Test Method D3828 is also based on the use of a 2-mL sample but notes that some models require a 4-mL sample. ISO 3679 specifies the use of a 2-mL sample for flash points up to 100°C and a 4-mL sample for flash points above that temperature. ASTM Test Method E502 allows various types of apparatus and defers to the two ASTM methods noted above when the small-scale closed-cup apparatus is used.

A timing device is incorporated in the small-scale apparatus. Both ASTM Test Methods D3278 and D3828 specify that 1 min shall elapse after injection of the test specimen prior to checking whether the conditions lead to a flash point. ISO 3679 specifies the 1-min time for flash points below 100°C but changes to a 2-min waiting period for flash points above that temperature. ASTM Test Method E502 goes even further and states, "Determine the flash points in the Setaflash unit using a holding time of 6 min at the test temperature instead of the 1 or 2 minutes normally employed." (Note that the Setaflash was a trade name now replaced by the use of "small-scale closed-cup apparatus" designation.)

ASTM Test Method D3941was first published in 1980 by ASTM Committee D01 on Paint and Related Coatings, Materials, and Applications [11]. This is an equilibrium method using the test cups complete with lid as specified in ASTM Test Methods D56 (Tag closed cup) and D93 (Pensky-Martens closed cup), which are placed in a separate water bath. “A specimen is heated in a closed cup of standard design in a suitable liquid bath at the rate of 1.0°F (0.5°C) in not less than 1.5 minutes” so that the difference in temperature between the specimen in the cup and bath never exceeds 3.5°F (2.0°C). Flash determinations are made at intervals of not less than 1.5 min or more than 5 min. The test cup is immersed in the liquid bath with the surface of the specimen in the cup at the same level as, or below, that of the liquid in the bath. Note also that the heating rate is slower than that specified in the dynamic test methods described earlier. The ignition test cycle is specified as taking 2.5 ± 0.5 s. Other details may be found in the standard.

Flash/No-Flash Tests

In some instances, it is more important to know whether or not a substance produces a flash at a specified temperature rather than to establish the finite flash point temperature. For example, specifications for a product may set a minimum temperature at which the product may flash, or government or other safety regulations may establish different categories of safety depending upon whether the substance flashes below or above a given temperature. Theoretically, any closed-cup flash point tester could be used in a flash/no-flash mode but, in reality, the small-scale tester is often the apparatus specified.

Four test methods that include flash/ no-flash procedures are ASTM Test Methods D3278, D3828, D3934, and ISO 3680 [12,13]. The first two contain both finite and flash/no-flash procedures; the last two are strictly flash/no-flash methods. ASTM Test Method D3934 is the only one of the four that does not use the small-scale tester. Instead, it uses the cups, complete with lids, of ASTM Test Methods D56 (Tag closed cup) or D93 (Pensky-Martens closed cup) along with a liquid bath capable of being adjusted to the required specification temperature.

The following summary is typical of the test procedure used with the small-scale apparatus. It is based upon the procedure given in ASTM Test Method D3828. Details will differ from test method to test method, so it is essential to follow the details of the test method specified. First, adjust the specified flash/no-flash temperature on the basis of the local barometric pressure. (The effect of barometric pressure on flash point will be discussed later in this chapter.) Inspect (for cleanliness) the sample cup, lid, and shutter mechanism of the instrument recommended by the manufacturer for the target flash point and put cover in place. For target temperatures above ambient, adjust the temperature of the apparatus to the target temperature. Using a syringe, inject a 2-mL (4-mL if using a high-range tester or testing above 100°C) test specimen into the test cup. After 2 min, apply the test flame over a 2.5-s cycle while watching for a flash. Record as either “flash” or “no flash.” For target temperatures below ambient, use a refrigerant-charged cooling block to cool the sample cup to about 10°C (18°F) below the target temperature before injecting the test specimen that has also been precooled. Allow the temperature to increase under ambient conditions until the target temperature is reached. Then apply the test flame as above and watch for a flash. As above, report either “flash” or “no flash.”

In ASTM Test Method D3934, which uses either the Tag or the Pensky-Marten cup with lid, the test cup is filled with the appropriate amount of test specimen at a temperature at least 20°F (10°C) below the specified test temperature corrected for barometric pressure. The cover is immediately placed on the cup, and the cup with lid is immersed in direct contact with the water in the heating bath and with the surface of the specimen in the cup at the same level as the liquid in the bath. The temperature of the test specimen is adjusted to within 1°F (0.5°C) of the corrected test temperature and held at this temperature for 10 min. The test flame is then applied over a 2.5-s cycle and the operator watches to see if there is a flash. The test is repeated using a fresh test specimen.

Continuously Closed-Cup Tests

ASTM Test Method D6450 (CCCFP), was first published by ASTM in October 1999 [14]. It is a dynamic method for the determination of the flash point of fuel oils, lube oils, solvents, and other liquids. The apparatus in this test method is an automated tester that uses a continuously closed but unsealed cup with air injected into the test chamber between ignition tests.

The lid of the test chamber is regulated to a temperature at least 18°C below the expected flash point. A test specimen of 1 ± 0.1 mL is introduced into the sample cup, along with a stirring magnet, after checking that the sample and the cup are both at least 18°C below the expected flash point. (The sample and the cup are cooled if necessary.) The cup is then raised and pressed into the lid to form the continuously closed but unsealed test chamber, which has an overall volume of 4.0 ± 0.2 mL. The temperatures of the specimen and the regulated lid are allowed to equilibrate, before the lid is heated at 5.5° ± 0.5° C/min. An arc of 3 ± 0.5 mJ is applied at 1°C intervals. After each ignition trial, 1.5 ± 0.5 mL of air is introduced into the test chamber to provide sufficient oxygen for the next flash trial. The pressure inside the test chamber is monitored automatically immediately after each arc discharge. When the pressure increase exceeds 20 kPa within 100 ms, the temperature of the test specimen at that time is recorded as the uncorrected flash point. This temperature is corrected for the ambient barometric pressure to obtain the flash point temperature.

When the expected flash point of a test specimen is unknown, a preliminary test is conducted setting the initial temperature at 10°C. The result of this preliminary test is used as the expected flash point for testing a fresh specimen of the sample.

When tests on samples contaminated with small concentrations of material with a much lower flash point revealed that ASTM Test Method D6450 yielded flash points as much as 8°C higher than flash points obtained using ASTM Test Method D93 Procedure A (Pensky-Martens closed- cup apparatus), a modified CCCFP apparatus and test method was developed to address the problem. This modified CCCFP method is now designated as ASTM Test Method D7094 (MCCCFP) [15]. The modified apparatus has a larger sample cup (7 mL). The test procedure is much the same as that of ASTM Test Method D6450, but a 2-mL test specimen is used rather than a 1-mL specimen, the heating rate is slower (3.5°C/min vs. 5.5°C/min), and a variable amount of air is used (larger volumes of air are used at high test temperatures). An interlaboratory test program has shown very good correlation of ASTM Test Method D7094 results with the ASTM Test Method D93A procedure results.

BAROMETRIC CORRECTIONS

When the uncorrected flash points are determined at two locations on test specimens from the same sample, different results are obtained if the ambient barometric pressures are different. Thus, laboratories located at high elevations (for example, in Denver) will generate lower uncorrected flash points than laboratories located at sea level (for example, New York City). To compare results at two such laboratories at different elevations, a barometric correction must be applied. As we have previously noted, there are two ways in which barometric corrections are applied. When determining finite flash points, a flash point correction must be added to the results obtained at the higher elevation to convert those results to the equivalent of sea level determinations. When conducting a flash/no-flash determination, the specification or other target flash point must be reduced at the higher elevation to be certain said target flash point is met at the sea level standard location. Corrections may be calculated from equations given in the various test methods. (Only ASTM Test Method D3143 of those mentioned in this chapter fails to call for a barometric correction and to provide equations.) The various equations provide atmospheric pressures measured in various units, and temperatures in either Celsius or Fahrenheit. In ASTM standards, equations call for ambient pressures measured in kilopascals or in millimeters of mercury.

The following equations for correcting the observed finite flash point are given in Test Method D56 and other ASTM standards:

$$\text{Corrected flash point} = C + 0.25(101.3 - p) \qquad (7.1)$$

$$\text{Corrected flash point} = F + 0.06\ (760 - P) \qquad (7.2)$$

$$\text{Corrected flash point} = C + 0.033\ (760 - P) \qquad (7.3)$$

In these equations, C is the observed flash point in degrees Celsius, F is the observed flash point in degrees Fahrenheit, p is the ambient barometric pressure in kilopascals at the laboratory at the time of test, and P is the ambient barometric pressure in millimeters of mercury at the laboratory at the time of test. A fourth equation is given in ISO standard DIS 13736 (the Abel apparatus):

$$\text{Corrected flash point} = C + 0.025\ (1013 - M) \qquad (7.4)$$

This equation is for the ambient barometric pressure (M) measured in hectopascals or millibars. Note that these equations result in the addition of a flash point correction value when the ambient barometric pressure at the time of test is less than one atmosphere (sea level). Using equation (7.1), we see that every 10-kPa decrease in pressure below the nominal sea level pressure of 101.3 kPa results in a 2.5°C flash point correction value that must be added to the observed flash point to get the equivalent sea level flash point.

For flash/no-flash determinations, ASTM Test Method D3278 presents four equations to correct a specification or target flash point for deviations in barometric pressure from sea level. With corrections in symbols to be consistent with those above, they are:

$$\text{Corrected target flash point } (^\circ\text{F}) = S - 0.06\ (760 - P) \qquad (7.5)$$

$$\text{Corrected target flash point } (^\circ\text{C}) = T - 0.03\ (760 - P) \qquad (7.6)$$

$$\text{Corrected target flash point } (^\circ\text{F}) = S - 0.42\ (101.3 - p) \qquad (7.7)$$

$$\text{Corrected target flash point } (^\circ\text{C}) = T - 0.23\ (101.3 - p) \qquad (7.8)$$

In these equations, P and p are, as above, barometric pressures measured in millimeters of mercury or kilopascals, respectively, S is the specification or sea level target flash point in degrees Fahrenheit, and T is the specification or sea level target flash point in degrees Celsius. ASTM Test Method D3934 cites the same four equations. ASTM Test Method D3828 cites only the equivalents of equations 7.5, 7.6, and 7.8, the last with a constant of 0.25 rather than 0.23 as given above, a minor difference. ISO 3680 cites only one equation, the equivalent of equation 7.8, but with the same 0.25 constant is used by Test method ASTM Test Method D3828. As an example, using equation 7.7, we see that the target temperature must be decreased by 4.2°F for every decrease in barometric pressure of 10 kPa.

CALCULATIONS AND REPORTING OF RESULTS

Calculations

There are three types of calculations specified in the various test method standards. The first is the correction of finite flash points (and flash point targets in flash/no-flash tests) for laboratory ambient barometric pressures other than sea level pressures of 101.3 kPa (760 mmHg), as discussed above. The others deal with the averaging of multiple determinations and with the rounding of results.

The various test methods for finite flash point give specific instructions for such calculations and for reporting results. These, summarized in Table 7.3, necessitate such calculations as obtaining the mean of multiple determinations in some methods and, in most methods, the rounding of the results after correcting for barometric pressure. The rounding is done after any averaging (determination of mean).

Reporting Results

The ISO standards tend to specify in greater detail what is to be included in the test report. Thus, to report finite flash points, ISO DIS 13736 (Abel) specifies that the report shall contain at least five things, specifically, (1) the test standard used, (2) the complete identification of the sample, (3) the result of the test expressed as noted in Table 7.3, (4) any deviations from the specified procedure, and (5) the date of the test. ISO 3679 also includes, by reference to a previous clause, the test interval and the barometric pressure at the time of the test. ASTM Test Method E502 requires reporting many of these same items but also specifies a statement regarding the purity of the material if known and any special preparation of the sample. Further, ASTM Test Method E502 requires a notation if no flash point was obtained in the course of the test, either "no flash to boiling at ____°C (°F)" or "no flash to ____°C (°F)." ASTM Test Method D1310, one of the test methods where more than one determination is required to obtain a mean flash point, states: "Report the mean of not less than three corrected recorded tests, other than the initial test, to the nearest 1°F (0.5°C). Three

TABLE 7.3—Summary of Finite Flash Point Calculations Other than Barometric Correction

STM	Apparatus	Calculation
ASTM		
D56	Tag CC	Round result to nearest 0.5°C (or 1°F)
D92	Cleveland OC	Round result to nearest 1°C (2°F)
D93	P-M CC	Round result to nearest 0.5°C (1°F)
D1310	Tag OC	(1) Round to nearest 1°F (0.5°C)
		(2) Average not less than three tests; round
D3278	Small-Scale CC	(1) Average duplicate tests
		(2) Round to nearest 0.5°C (1°F)
D3828	Small-Scale CC	(1a) Round to nearest 1°C (2°F)
		(1b) Round to nearest 0.5° (1°F)
D3941	D56 or D93 Cup	(1) Average two results
		(2) Round to nearest 1°F (0.5°C)
D6450	CCCFP	Round corrected value to nearest 0.5°C
D7094	MCCCFP	Round corrected value to nearest 0.5°C
E502	TagCC, P-MCC, or Setaflash CC	Round average downward to nearest whole number
ISO 12736	Abel	Round to nearest 0.5°C
D3679	Small-Scale CC	Round to either nearest 0.5° or 1.0°C

CC = closed cup; OC = open cup; P-M = Pensky-Martens.

multiple runs are acceptable for averaging if the difference between the extreme values does not exceed 7°F (4°C) (95 % confidence level).” ASTM Test Method D3278, which includes both a flash/no-flash method (Method A) and an actual finite flash point method (Method B), specifies that the latter, the finite flash point, shall be reported as “the mean of duplicate determinations to the nearest 0.5°C (1°F), provided the difference between the values does not exceed 1°C (2°F) and that Test Method B was used.” Because there are differences in reporting among the methods, be careful to report all required information for the specific method used.

For flash/no-flash test methods, the ISO standards again tend to require reporting more details. Thus ISO 3680 calls for the inclusion of the standard used, the type and complete identification of the product tested, the result of the test as specified in an earlier clause, any deviations from the test procedures, and the date of the test. The “earlier clause” requires the reporting of the specified flash/no-flash temperature, or the test flash/no-flash temperature, corrected to the standard atmospheric pressure of 101.3 kPa, rounded to the nearest 0.5°C and whether there was a flash or no flash. The clause also requires reporting the ambient barometric pressure in the vicinity of the apparatus and the reporting of whether there was a continuous luminous flame present in the orifice of the apparatus. In contrast, ASTM Test Method D3828 calls for reporting flash (or no flash) at the target temperature and that Method A (the flash/no-flash procedure in the method) was used.

SUMMARY

The basic procedures for the various types of test method were described. These covered the old dynamic manual methods, automated versions of those methods, the finite equilibrium methods, the flash/no-flash methods, and finally the continuously closed-cup method. Corrections for ambient barometric pressures other than the standard atmospheric pressure of 101.3 kPa (760 mmHg) were given. Finally, other calculations and the nature of the report were covered.

REFERENCES

[1] ASTM D56, “Standard Test Method for Flash Point by Tag Closed Cup Tester,” *ASTM Book of Standards,* ASTM International, West Conshohocken, PA.

[2] ASTM D92, “Standard Test Method for Flash and Fire Points by Cleveland Open Cup Tester,” *ASTM Book of Standards,* ASTM International, West Conshohocken, PA.

[3] ASTM D93, “Standard Test Method for Flash Point by Pensky-Martens Closed Cup Tester,” *ASTM Book of Standards,* ASTM International, West Conshohocken, PA.

[4] ASTM D1310, “Standard Test Method for Flash Point and Fire Point of Liquids by Tag Open Cup Apparatus,” *ASTM Book of Standards,* ASTM International, West Conshohocken, PA.

[5] ASTM D3143, “Standard Test Method for Flash Point of Cutback Asphalt with Tag Open Cup Apparatus,” *ASTM Book of Standards,* ASTM International, West Conshohocken, PA.

[6] ISO/DIS 13736, “Petroleum Products–Determination of Flash Point–Abel Closed Cup Method,” *International Organization for Standardization,* Geneva, Switzerland.

[7] ASTM E502, "Standard Test Method for Selection and Use of ASTM Standards for the Determination of Flash Point of Chemicals by Closed Cup Methods," *ASTM Book of Standards,* ASTM International, West Conshohocken, PA.

[8] ASTM D3278, "Standard Test Method for Flash Point of Liquids by Small Scale Closed-Cup Apparatus," *ASTM Book of Standards,* ASTM International, West Conshohocken, PA.

[9] ASTM D3828, "Standard Test Method for Flash Point by Small Scale Closed Tester," *ASTM Book of Standards,* ASTM International, West Conshohocken, PA.

[10] ISO 3679, "Determination of Flash Point—Rapid Equilibrium Closed Cup Method," *International Organization for Standardization,* Geneva, Switzerland, 1983.

[11] ASTM D3941, "Standard Test Method for Flash Point by the Equilibrium Method with a Closed-Cup Apparatus," *ASTM Book of Standards,* ASTM International, West Conshohocken, PA.

[12] ASTM D3934, "Standard Test Method for Flash/No Flash Test–Equilibrium Method by Closed-Cup Apparatus," *ASTM Book of Standards,* ASTM International, West Conshohocken, PA.

[13] ISO 3680, "Determination of Flash/No Flash–Rapid Equilibrium Closed Cup Method," *International Organization for Standardization,* Geneva, Switzerland, 1983.

[14] ASTM D6450, "Standard Test Method for Flash Point by Continuously Closed Cup (CCCFP) Tester," *ASTM Book of Standards,* ASTM International, West Conshohocken, PA.

[15] ASTM Standard D7094, "Standard Test Method for Flash Point by Modified Continuously Closed Cup (MCCCFP) Tester," *ASTM Book of Standards,* ASTM International, West Conshohocken, PA

8

Precision of Flash Point Test Methods

INTRODUCTION AND BACKGROUND

For approximately the last half century, ASTM has required a statement regarding precision and bias in every standard test method. The *ASTM Form and Style Manual* defines precision as the closeness of agreement between test results obtained under prescribed conditions. Note that precision statements are mandatory for any ASTM test method that produces a test result. The *Form and Style Manual* also defines bias as a systematic error that contributes to the difference between the mean of a large number of test results and an accepted reference value. Because all flash point test methods are empirical, i.e., the test results are defined only by the test method, there is no bias *per se*; hence, statements to that effect are not found in all cited ASTM methods. The matter of relative bias, i.e., the difference between the flash points obtained with manual and automated equipment, and the differences between the flash points obtained by the various test methods, will be discussed in Chapter 9.

The primary intent of this chapter is to present a listing of the precision indicated in the various flash point test methods and to identify the nature of the samples on which those precision values are based. However, because some readers may be unfamiliar with statistics and some may be a bit rusty in that regard, the chapter will start with brief overviews of the precision of measurements and the way precision values are obtained.

EXPERIMENTAL ERRORS

From an analytical point of view, every time a standard test method is run, it, like all experiments, is subject to errors. Measurement errors are of two types: random errors and systematic errors. Random errors in experimental measurements are caused by unknown and unpredictable changes in the measurement process. These changes may occur in the measuring instruments or in the environmental conditions under which the test is conducted or in the reading of gauges, burettes, thermometers, etc. Systematic errors in experimental measurements usually come from the measuring instruments. They may occur because there is something wrong with the instrument or its data-handling system, or the instrument is used improperly by the analyst.

From a practical point of view, there are errors associated with the test operator or analyst that can be called "operator errors." Examples of such errors are transcription errors in transferring data from scraps of paper or notebooks to the official logs, as well as such errors as "graphite analyses," where the analyses were not done but the data were penciled into the log and "good as" substitution error caused by deviating from the prescribed test method.

Operator errors should not occur, but they do. Early in his career (some 40 years ago), the author picked out one transcription error when the resultant data did not fit an otherwise smooth curve. On checking the original data, the mistake was obvious. (The figure "1" had been transcribed as the figure "7.") The author has also experienced several examples of "graphite analyses" or deliberate "manufacturing of data." When challenged, the operator said there was no use in wasting time to conduct the analysis when the result was always the same. He missed the point that the analysis was conducted to ensure the result was within the variation associated with "common causes," i.e., within operational requirements.

The author has also experienced several instances of "good as" errors. In one case, the specified filtration technique was replaced with another and in another case, a solvent was evaporated in a porcelain dish on a hot plate rather than by the prescribed method. In both cases, the analyst did not have the specified equipment available and felt the substituted method was "just as good as" the method specified. Regardless of whether a comparison of the two methods might have shown the same result and precision, the substitution meant that the analyst was no longer running the standard test method.

If due care is taken to preclude operator errors, any determination of a flash point by a particular method is still subject to random errors. These would include such things as the rate of temperature increase, the reading of the thermometer or temperature-sensing system, the time of application of the ignition source, and even the way the sample is stored and transferred. However, such errors are as likely to be positive as negative in effect. If a number of repetitions of the test are run, the results could be shown in a histogram such as Figure 8.1 and a normal frequency curve (the bell-shaped Gaussian distribution curve) can be fitted to the data. The greater the number of data points, the better will be the fit of the curve.

ESTIMATING PRECISION

An interlaboratory study (ILS) program is used to arrive at an estimate of the precision of any ASTM test method. Details for conducting such a program (called an ILS or round robin) to determine the precision and bias of a test method may be found in ASTM documents such as ASTM Standard Practice E691 and ASTM Standard Practice D6300 [1,2]. Standard Practice D6300 is under the jurisdiction of Committee D02 on Petroleum Products and Lubricants and is limited to use with homogeneous samples, where, with due care, serious problems with sampling do not normally occur. Other ASTM committees may have their own standard practices dealing with precision.

The following summarizes a six-step program for conducting a round robin according to ASTM Standard Practice D6300:

Step 1: A draft of the test method is prepared. A pilot is conducted with at least twelve laboratory and sample combinations to reveal problems in interpreting or conducting the test method as written and to provide preliminary estimates of precision and bias. The samples should cover the range of the property to be measured.

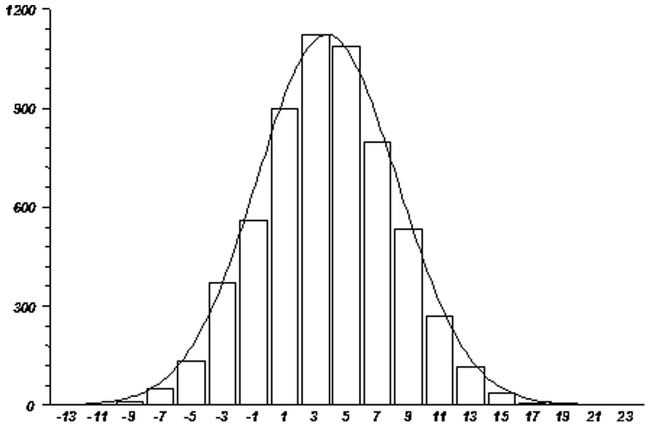

Figure 8.1—Histogram fitted with Gaussian distribution curve.

Step 2: The draft of the test method is revised (if necessary), participating laboratories are recruited, and the number of samples (covering the range of the property to be measured) are determined from the preliminary precision values and are obtained.

Step 3: The revised test method, the samples, blank forms for submitting data, the order of testing samples, and other instructions are distributed to the participating laboratories.

Step 4: The round robin is run during a specified time frame, and all data are sent to the person overseeing the program.

Step 5: The data are examined for abnormalities and checks are made for outliers and uniformity. Precision values are estimated.

Step 6: Finally, in ASTM practice, the results of the interlaboratory program are assembled in a research report, approved by committee members, and filed at ASTM headquarters.

THE PRECISION VALUES

Two measures of precision are required in an ASTM test method that produces a test result, i.e., the repeatability and the reproducibility. A third precision value (determinability) is sometimes required, when averaging two or more determinations to obtain the reported result. These precision parameters are defined as:

repeatability, *n.*–The difference between successive results obtained by the same operator with the same apparatus under constant operating conditions on identical test material will, in the long run, in the normal and correct operation of the test method exceed the repeatability only in 1 case in 20.

reproducibility, *n.*–The difference between 2 single and independent results obtained by different operators working in different laboratories on identical test material using instruments of the same design will, in the long run, exceed the reproducibility in only 1 case in 20.

determinability, *n.*–the difference between a pair of determined values (for use in obtaining an average value as a test result) will, in the long run, exceed the determinability in only 1 case in 20.

The expression "1 case in 20" does not mean that there will be 1 value exceeding that precision measure in every 20 cases. Rather, about 95 % of the time, the difference between 2 results under repeatability/reproducibility will be within the published repeatability/reproducibility value.

PRECISION VALUES OF FLASH POINT METHOD

The precision values (r and R) given in a number of ASTM standard flash point methods are shown in Table 8.1, and those given in International Standardization Institute (ISO) flash point methods are shown in Table 8.2.

THE BASES OF FLASH POINT PRECISIONS

As stated previously, ASTM precision are obtained through interlaboratory programs in which a number of laboratories test a set of samples. Strictly speaking, the resultant precision values are applicable only for the types of materials (samples) and for the range of the measured property included in the ISL. As a consequence, it is important to know the details of any interlaboratory program. Therefore, information on the number of laboratories, and the number and general nature of the samples is summarized in Table 8.3. Additional details are provided in the subsequent discussion.

ADDITIONAL INFORMATION

ASTM Test Method D56 (Tag Closed Cup)

ASTM Research Report S15-1007 states that the precision values for ASTM Test Method D56 were developed in 1991 using 8 samples and 22 laboratories, with 12 laboratories using manual equipment and 17 using automated equipment [3,4]. The 8 samples were: low aromatic mineral spirits, amyl alcohol, diacetone alcohol, dimethyl formamide, mineral spirits, o-dichlorobenzene, glycol ether acetate, and isoparaffinic solvent.

ASTM Test Method D92 (Cleveland Open Cup)

ASTM Research Report S15-1009 states that the precision values for flash point were established in a 1991 program using seven samples with five laboratories using manual equipment and eight laboratories using automated equipment [5,6]. All seven samples were Amoco products identified as White Oil (a light lube oil for small motors), LDO 10W30 (a multigrade long-distance oil), 1000 Fluid (a transmission fluid), 13 NF Mineral Oil (a food-grade mineral oil), Wax Tac 68 (a heavy-duty lube oil for machinery), Worm Gear Oil (a heavy-duty gear oil), and AC 10 (an asphalt cut).

ASTM Test Method D93 (Pensky-Martens Closed Cup)

This method consists of three distinct procedures [7]. Procedure A is applicable to distillate fuels, unused lubricating oils, and other homogeneous petroleum liquids, whereas Procedure B is applicable to residual fuels and "other types" such as petroleum liquids containing solids, liquids forming surface films under test conditions, cutback residua, and used lubricating oils Procedure C is for biodiesel fuels.

Procedure A: ASTM D93 states that the precision measures for Procedure A were derived on clear liquids only and that they were derived from a combined 1991 cooperative test program described in ASTM Research Report S15-1008 and a 1994 program of the Institute of Petroleum (now the Energy Institute) [8].

The ASTM 1991 interlaboratory test program used five samples of fuel and lubricating oil with twelve laboratories using manual apparatus. Seven samples were issued, but due to excessive missing data or to excessive outlier cells as determined by the Hawkins test, only five were used in the final statistical evaluation. The five samples used were a hydrocarbon-based solvent, light cycle oil, no. 2 diesel, no. 2 fuel oil, and a base oil stock. Flash points for the first four

TABLE 8.1—Repeatability (r) and Reproducibility (R) of ASTM Flash Point Methods

Test Method	Applicability	r °C	R °C
D56 Tag CC	<60°C	1.2	4.3
	>60°C	1.6	5.8
D92 Cleveland OC		8	18
D93 Pensky-Martens CC			
Procedure A		0.029X	0.071X
Procedure B	Residual F.O.	2	6
	Other	5	10
D1310 Tag OC		2	4
D3143 Tag OC		10	15
D3278 Small Scale	<45 SUS	2.7	3.3
	>45 SUS	3.3	5
D3828 Small Scale	20°–70°C	0.5	0.03(M + 24)
	>70°C	$0.022\ M^{0.9}$	$0.083\ M^{0.9}$
D3941 Equilibrium CC		2	3
D6450 CCCFP		1.9	3.1
D7094 MCCCFP		4.1	5.5
E502		[a]	[a]

CC=closed cup; OC=open cup; CCCFP=continuously closed-cup flash point; MCCCFP=modified continuously closed-cup flash point; F.O.=fuel oil; X=the average of the results being compared in °C; M=mean of two results in °C; SUS=Saybolt Seconds Universal.

[a] The author has been advised that the precision measures are being adjusted to conform with the test methods cited in E502.

TABLE 8.2—Repeatability and Reproducibility of ISO Flash Point Methods

ISO Method	Material/Range	r °C	R °C
DIS 1523 Equilibrium CC	Paints, Petroleum et al.		
	30°–100°C	2.0	3.0
DIS 3679 Rapid	Petroleum & Related		
	20°–70°C	0.5	0.03(X + 29)
	>70°C	$0.022X^{0.9}$	$0.083X^{0.9}$
	Paints, Enamels, etc.		
	< 5.8 mm^2/s	1.7	3.3
	> 5.8 mm^2/s	3.3	5.0
	FAME	1.9	15.0
DIS 13736 Abel	Petroleum Products et al.	1.0	1.5

X = the average of the results being compared in °C; FAME = fatty acid methyl esters.

ranged from 60°–102°C, but the fifth sample had a much higher flash point (202°–207°C).

Table 8.4 shows values at 10°C intervals calculated from these two ASTM Test Method D93 precision expressions.

Procedure B: The precision data for Procedure B for residual fuels were developed in a 1996 cooperative program conducted by the Institute of Petroleum (now the Energy Institute) using 12 residual fuel oils and "other types," with 40 laboratories worldwide using both the manual and automated apparatus. The "other types" have not been specifically defined but are assumed to have been such materials as petroleum liquids containing solids, those forming surface films under test conditions, cutback residua, or used lubricating oils as specified in the scope of Procedure B.

Procedure C: See current version of D93 for information regarding precision of Procedure C.

TABLE 8.3—Summary of Interlaboratory Programs

STM	Apparatus	Research Report	No. Labs	No. & Type Samples
D56	Tag CC	S15-1007	22	8 Solvents
D92	Cleve. OC	S15-1009	8	7 Lubes and oils
D93-A	P-M CC	S15-1008	21	5 Fuel oils and lubes
		IP Program	26	12 Fuels and 4 chemicals
D93-B	P-M CC	IP Program	40	12 Residual fuels
D1310	Tag OC	D01-1002	8	2 Paint solvents
				2 Glycol and diol
D3278	Small Scale	D-1-1000	5	4 Solvents and 5 resins
D3941	Equil. CC	Cites ISO		
D6450	CCCFP	D02-1464	9	10 Fuels, lubes et al.
D7094	MCCCFP	D02-1581	8	17 Fuels, lubes et al.

Cleve.=Cleveland; P-M=Pensky-Martens; IP=Institute of Petroleum (now the Energy Institute); Equil.=Equilibrium.

TABLE 8.4—Test Method D93 Calculated Precision

Average Flash Point	Repeatability = 0.029X	Reproducibility = 0.071X
X in °C	°C	°C
60	1.74	4.26
70	2.03	4.97
80	2.32	5.68
90	2.61	6.39
100	2.90	7.10
110	3.19	7.81
120	3.48	8.52
130	3.77	9.23
140	4.06	9.94
150	4.35	10.65
160	4.64	11.36
170	4.93	12.07
180	5.22	12.78
190	5/51	13.49
200	5.80	14.20
210	6.09	14.91

It is understood that the residual fuel data were evaluated by ISO 4259, which is equivalent to ASTM Standard Practice D6300.

ASTM Test Method D1310 (Tag Open Cup)

This method, under the jurisdiction of ASTM Committee D01 on Paint and Related Coatings, Materials, and Applications, presents three cases of precision values [9]. Case 1 covers flash points between 0° and 200°F (−18° and +93°C); Case 2 covers flash points between 200° and 325°F (93° and 165°C); and Case 3 covers flash points of viscous, heavily pigmented materials that tend to form a surface film.

ASTM Research Report D01-1002 indicates the precision values were obtained from an analysis of variance of data obtained in an ISL [10]. For Case 1 (the low-flash case), two samples (vinyl acetate and *n*-heptane) were used with one analyst in each of eight laboratories performing five multiple determinations on each sample, and repeating on a second day. For Case 2 (the high-flash case), two samples (diethylene glycol and 2-ethylhexanediol-1,3) were used with one operator in each of ten laboratories performing five multiple determinations and repeating on a second day.

Although ASTM Test Method D1310 states that Case 3 precision values were based on an ISL, there are no data in ASTM Research Report D01-1002 for viscous, highly pigmented materials. However, the precision cited tends to be poorer at higher flash point levels and when heavily pigmented materials that tend to form surface films are involved.

ASTM Test Method D3143 (Cutback Asphalt with Tag Open Cup)

This method applies to cutback asphalts with flash points less than 93°C [11]. Although no research report is cited in the method, the user is informed that the single operator standard deviation has been found to be 3.7°C, and, therefore, results of two properly conducted tests by the same operator on the same asphalt should not differ by more than 10°C. The user is also advised that the multilaboratory standard deviation has been found to be 5.4°C, and, therefore, that results of two properly conducted tests from two different samples of the same asphalt should not differ by more than 15°C.

ASTM Test Method D3278 (Small-Scale Closed Cup)

This standard of ASTM Committee D01 on Paint and Related Coatings, Materials, and Applications incorporates both flash/no-flash (Test Method A) and finite flash point (Test Method B) procedures [12]. Both Test Method A and Test Method B have two subprocedures: (1) ambient to 110°C (230°F), and (2) 0°C (32°F) to ambient temperature. There is, of course, no precision for Test Method A (Flash/No-Flash). The precision of Test Method B is stated separately for liquids with viscosities below 45 SUS and those with viscosities above that level. The former applies to solvents and the latter to resins, paints, and liquids with dispersed solids.

In an ISL of Test Method B, one operator in each of five laboratories made two determinations on two different days on four solvents, three resins, and two paints of different flash points ASTM Research Report D01-1000 provides additional information on the round-robin study [13]. The four solvents used in the study were toluene, *p*-xylene (standard), Stoddard solvent, and an “odorless solvent.” (Note: ASTM Specification D235 for Mineral Spirits [Petroleum Spirits] [Hydrocarbon Dry Cleaning Solvent] states that “Stoddard solvents” is the term used when mineral spirits are used for dry cleaning [14]. ASTM Specification D235 also indicates that only products that have a very high isoparaffin content approaching 100 % are considered to fit the odorless category. ASTM Specification D3735 [VMP Naphthas] makes a similar statement about the Type III Odorless category [15]).

The five resins and pigments were described as: (1) alkyd, gum modified; (2) epoxy resin; (3) acrylic resin; (4) automotive refinish black; and (5) DCO epoxy ester. Research Report D-1-1000 indicates that, although seven laboratories participated in the round robin, insufficient data were received from two of the laboratories. Only the data of the remaining five were used in the statistical analysis.

ASTM Test Method D3828 (Small-Scale Closed Tester)

This method uses the same type of closed-cup tester as ASTM Test Method D3278 but is under the jurisdiction of Committee D02 on Petroleum Products and Lubricants [16]. The number and nature of the samples used in obtaining the precision values presented in the test method and the number of laboratories involved in the interlaboratory program are not indicated in the standard. However, when the referenced Research Report D02-1214 is examined, it appears that the precision values were based on a round robin incorporating *p*-xylene and paint as well as Committee D02 types of materials, i.e., Avtur, premium kerosine, Avcat, and gas oil [17]. Avtur is what Committee D02 calls Jet A1, and Avcat was a widecut aviation fuel comparable to the military JP5.

ASTM Test Method D3941 (Closed-Cup Equilibrium Method)

This method is under the jurisdiction of ASTM Committee D01 on Paint and Related Coatings, Materials, and Applications [18]. The test method is said to be similar to ISO 1523 but uses standard ASTM cups, style, and format. Test cups from ASTM Test Method D56 (Tag closed cup) and from ASTM Test Method D93 (Pensky-Martens closed cup) are cited. ASTM Test Method D3941 cites the precision values from the comparable ISO standard. (See the discussion of ISO 1523.)

ASTM Test Method D6450 (Continuously Closed-Cup Tester)

This method is under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants [19]. It covers the determination of flash points of fuel oils, lube oils, solvents, and other liquids with flash points ranging from 10°–250°C.

The precision of the method was developed in a 1996 interlaboratory test program involving nine laboratories operating the CCCFP apparatus. The precision data are said to exclude data from a no. 6 fuel oil sample. ASTM Research Report D02-1464 states that the round robin used anisole of 99.7 % purity with a nominal flash point of 43°C as a verification fluid [20].

The samples used in the interlaboratory program included three pure substances (2-propanol, 1-butanol, and *n*-methyl pyrrolidone), one hydrocarbon (*n*-dodecane), and six other products (jet fuel, diesel fuel, no. 6 fuel oil, two-cycle lubricating oil, solvent oil, and Optimol lubricating oil). The jet fuel was a Jet A kerosine fuel (F. Hutto e-mail of March 23, 2005) and is thought to have been a Jet A-1 fuel (R. Aschauer e-mail of March 15, 2005). The diesel fuel was a no. 2 diesel fuel, and the solvent oil was a paraffinic mineral oil containing dewaxed heavy paraffinic petroleum distillates (F. Hutto). The Optimol was a synthetic lubricant with a viscosity of 102 mm^2/s at 40°C.

ASTM Test Method D7094 (Modified Continuously Closed Cup)

The MCCCFP method is a dynamic method similar to that of ASTM Test Method D6450 but is designed for determining the flash point of fuels, lube oils, solvents, and other liquids [21]. It is under the jurisdiction of Subcommittee 8 on Volatility of ASTM Committee D02 on Petroleum Products and

Lubricants. The method is similar to that of D6450 but uses a larger cup (7 mL) and sample size (2 mL).

The standard indicates that the precision data were developed in a 2001 cooperative test program involving eight laboratories and using eleven fuels (both pure and contaminated), four lubricating oils (both pure and contaminated), and two pure chemicals. ASTM Research Report D02-1581 indicated that the pure fuels consisted of two conforming to Jet A requirements and three diesel fuels (probably 2-D, but not indicated), one from each of three refineries [22]. Four contaminated jet fuels were prepared by adding small volumes of gasoline or, in one case, biodiesel to samples of Jet A. Two contaminated diesel fuels were prepared by adding small volumes of regular motor gasoline to two of the pure diesel fuels. The pure lubricating oils consisted of one from each of two sources, a two-stroke oil, and one of the pure lubricating oils to which a small volume of diesel fuel was added. Two pure chemicals were also included, i.e., anisole, which was provided as a blind sample, and dodecane, which each laboratory obtained locally.

ASTM TEST METHOD E502 FOR CHEMICALS

This method is under the jurisdiction of ASTM Committee E27 on Hazard Potential of Chemicals [23]. The apparatus may be that of ASTM Test Methods D56 or D3941 (Tag closed cup), D93 (Pensky-Martens closed cup), or D3278/D3828 (small-scale closed tester), and the procedures are those of the respective test methods modified to provide temperature equilibrium. For example, the holding time of the small-scale tester is raised to 6 min from the 1 or 2 min normally used. A basis for selecting one apparatus over another is given, with viscosity and flash point of the sample as the criteria.

ASTM Test Method E502 states that its precision is that of the various methods. A footnote in the method indicates that, although the data obtained in an interlaboratory program were of insufficient magnitude to establish alternative precision values, they did indicate that the precision values for chemicals are within those of the basic methods.

ASTM Research Report E27-1000 lists the chemicals used in the interlaboratory program as isopropanol, diethylene glycol monobutyl ether, dibutyl phthalate, diethylene glycol, and 2-ethyl hexanol [24]. Eight laboratories were included in the program. Each laboratory determined the flash point of isopropanol, diethylene glycol monobutyl ether, and 2-ethyl hexanol using a Tag closed-cup apparatus at a temperature rise rate of 2°F/min. Each laboratory also determined the flash point of diethylene glycol monobutyl ether, dibutyl phthalate, and diethylene glycol using a Pensky-Martens apparatus and a 10°F/min temperature rise rate. Each laboratory made one to four determinations on each sample. The research report noted that the standard deviation increased as the flash point temperature increased.

ISO/DIS 1523 (Closed-Cup Equilibrium Method)

This is a method to determine the flash point of paints, varnishes, paint binders, solvents, petroleum, or related products exclusive of waterborne paints [25]. It is similar to ASTM Test Method D3941, but it permits the use of Abel and Abel-Pensky cups in addition to the Tag closed cup and the D93 Pensky-Martens closed cup cited in the ASTM Test Methods D56 and D93, respectively. The repeatability (2°C) and the reproducibility (3°C) are the same as those cited in these ASTM standards. In fact, the latter cites the ISO work as the basis for its precision statements. There is no information on the basis of the values cited.

ISO/DIS 3679 (Rapid Equilibrium Closed-Cup Method)

This standard test method is used for the determination of the flash points of paints (including water-based paints, varnishes, paint binders, adhesives, solvents, petroleum, and related products having closed-cup flash points in the range from −30°C to +300°C [26]. Under specified conditions, it may also be used to determine the flash point of FAME. The test method uses an apparatus variously known as the rapid equilibrium tester or the Setaflash tester. A flash is indicated by a rise of 6.0°C detected within 100 ms.

The precision of the method is reported to be based upon the statistical examination of interlaboratory data on three matrices: (1) a matrix of petroleum and related products; (2) a matrix of paints, enamels, lacquers, varnishes, and related products with viscosities less than 150 mm^2/s at 25°C; and (3) a matrix of FAME products. The precision values shown in this standard for petroleum products are the same as those given in ASTM Test Method D3828.

The repeatability and reproducibility of the method when used with paints, enamels, lacquers, and varnishes were found to be the same as those cited by the comparable Committee D01 on Paint and Related Coatings, Materials, and Applications in ASTM Test Method D3278. The repeatability and reproducibility of the method when determining the flash point of FAME were found to be high.

ISO/DIS 13736 (Abel Closed Cup)

This standard test method uses the Abel closed-cup apparatus for flash points of petroleum products and other liquids having flash points between −30°C and +70°C [27]. Results, corrected for barometric pressure, are reported to the nearest 0.5°C. However, no information is given on the nature of the round robin samples used in obtaining the precision values.

USE OF TEST METHOD PRECISION VALUES

So far in this chapter, we have mentioned three precision parameters (determinability, repeatability, and reproducibility), and we have noted how these are estimated experimentally. We will now note some uses of these precision values. (See also ASTM Practice D3244 [28].)

Use of Determinability

Determinability is not a factor in most flash point test methods. Most flash point methods involve a single determination to obtain the flash point result. However, several flash point test methods do involve multiple determinations that are then averaged to obtain the flash point result. In those cases, the determinability is sometimes used to ascertain whether the spread among the multiple determinations is reasonable. The action to take if the specified value is exceeded is included as part of the test procedure. For example, ASTM Test Method D1310 calls for not less than three determinations and considers the three "acceptable for averaging if the difference between the extreme values does not exceed 7°F (4°C) (95 % confidence level)." This 95 % confidence level is, of course, the determinability.

Use of Repeatability

Although most flash point methods call for a single result, there are times when a result is outside the normal range for the type of product or where other reasons induce the analyst to repeat the test. If the two results differ by more than the published repeatability of the method, both results should be rejected (see Practice D3244 on utilization of test data). Two additional results are then obtained under conditions of repeatability, i.e., single operator, same apparatus, and constant operating conditions. If the difference between these two new results is less than the published repeatability, their average is considered applicable to the sample tested. However, if their difference again exceeds the repeatability, the results should again be rejected and the cause should be investigated. Deviations from the published procedure or an apparatus failure could be the cause.

Use of Reproducibility

Where a product is transferred, e.g., between a seller and a buyer, it is customary for a laboratory representing the seller and a laboratory representing the buyer to both conduct tests to confirm conformance to the purchase specification. If the difference between the single results obtained by the two laboratories is equal to or less than the published reproducibility, both results are considered acceptable and the assigned value is the average of the results from the two laboratories. When, however, the difference in the results obtained by the two laboratories exceeds the published reproducibility, both values are rejected and both laboratories repeat the test. If the difference between these two new results is now equal to or less than the published reproducibility value, the two values are averaged. If the difference between the two values is again greater than the reproducibility, both values are rejected and the possible cause (such as failure to follow the test method or equipment failure) is investigated.

SUMMARY

This chapter has briefly summarized causes of experimental errors in flash point determinations, defined three measures of precision (determinability, repeatability, and reproducibility), presented the precision values published for a number of flash point test methods, summarized some of the information available in research reports on the interlaboratory programs by which these precision measures were estimated, and discussed a few uses of the three measures of precision

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[3] ASTM D56, "Standard Test Method for Flash Point by Tag Closed Cup Tester," *ASTM Book of Standards,* ASTM International, West Conshohocken, PA.

[4] ASTM Research Report RR:S15-1007, "Interlaboratory Study on Manual and Automatic Tag Closed Cup Flash Point," submitted by R. G. Montemayor, May 27, 1993.

[5] ASTM D92, "Standard Test Method for Flash and Fire Points by Cleveland Open Cup Tester," *ASTM Book of Standards,* ASTM International, West Conshohocken, PA.

[6] ASTM Research Report RR:S15-1009, "Interlaboratory Study on Manual and Automatic Cleveland Open Cup Flash Point," submitted by R. G. Montemayor, May 27, 1993.

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[10] ASTM Research Report RR:D01-1002, "Supporting Data for D1310, Test for Flash Point of Liquids by Tag Open-Cup Apparatus," September 12, 1974.

[11] ASTM D3143, "Standard Test Method for Flash Point of Cutback Asphalt with Tag Open-Cup Apparatus," *ASTM Book of Standards,* ASTM International, West Conshohocken, PA.

[12] ASTM D3278, "Standard Test Method for Flash Point of Liquids by Small Scale Closed-Cup Apparatus," *ASTM Book of Standards,* ASTM International, West Conshohocken, PA.

[13] ASTM Research Report RR:D01-1000, "Test for Flash Point of Liquids by SetaFlash Closed Tester," submitted by H. A. Wray, July 30, 1973.

[14] ASTM D235, "Standard Specification for Mineral Spirits (Petroleum Spirits) (Hydrocarbon Dry Cleaning Solvent)," *ASTM Book of Standards,* ASTM International, West Conshohocken, PA.

[15] ASTM D3735, "Standard Specification for VMP Naphthas," *ASTM Book of Standards,* ASTM International, West Conshohocken, PA.

[16] ASTM D3828, "Standard Test Method for Flash Point by Small Scale Closed Tester," *ASTM Book of Standards,* ASTM International, West Conshohocken, PA.

[17] ASTM Research Report RR:D02-1214, untitled assortment of interlaboratory data dating from about 1977.

[18] ASTM D3941, "Standard Test Method for Flash Point by the Equilibrium Method with a Closed-Cup Apparatus," *ASTM Book of Standards,* ASTM International, West Conshohocken, PA.

[19] ASTM D6450, "Standard Test Method for Flash Point by Continuously Closed Cup (CCCFP) Tester," *ASTM Book of Standards,* ASTM International, West Conshohocken, PA.

[20] ASTM Research Report RR:D02-1464, "1996–1997 Continuously Closed Cup, Manual Pensky-Martens, and Automated Pensky-Martens Round Robin Flash Point Programs," submitted by F. Hutto and W. Grabner, February 25, 1998.

[21] ASTM D7094, "Standard Test Method for Flash Point by Modified Continuously Closed Cup (MCCCFP) Tester," *ASTM Book of Standards,* ASTM International, West Conshohocken, PA.

[22] ASTM Research Report RR:D02-1581, "Interlaboratory Test Study to Establish Precision for ASTM D7094," June 1, 2004.

[23] ASTM E502, "Standard Test Method for Selection and Use of ASTM Standards for the Determination of Flash Point of Chemicals by Closed Cup Methods," *ASTM Book of Standards,* ASTM International, West Conshohocken, PA.

[24] ASTM Research Report RR:E-27-1000, "Round Robin Data for E502, Test for Flash Point of Chemicals by Closed Cup Methods," May 22, 1973.

[25] ISO/DIS 1523, "Determination of Flash Point–Closed Cup Equilibrium Method."

[26] ISO/DIS 3679, "Determination of Flash Point–Rapid Equilibrium Closed Cup Method, International Organization for Standardization," Geneva, Switzerland, 2002.

[27] ISO/DIS 13736, "Petroleum Products–Determination of Flash Point–Abel Closed Cup Method, International Organization for Standardization," Geneva, Switzerland.

[28] ASTM D3244, "Standard Practice for Utilization of Test Data to Determine Conformance with Specifications," *ASTM Book of Standards,* ASTM International, West Conshohocken, PA.

9

Flash Point Relationships

INTRODUCTION

The flash point is the lowest temperature corrected to a pressure of 101.3 kPa (760 mm Hg) at which application of an ignition source causes the vapor of the specimen of the sample to ignite under condition of test. Among other things, the flash point is a function of the volatility of the material being tested, the apparatus design, and the test method procedure.

In this chapter, we explore some of these relationships. First, we discuss the barometric correction applied in the various test methods; second, we examine the bias between test methods; and finally, we explore the relationships between flash point and various measures of volatility, such as boiling point (for pure compounds) and the boiling range data (from simulated distillation) for mixtures.

THE BAROMETRIC CORRECTION

ASTM Test Method D93 using the Pensky-Martens apparatus presents three equations to correct the observed flash point temperature for the ambient barometric pressure [1]. The corrected flash point is given as equal to:

$$C + 0.25(101.3 - K) \tag{9.1}$$

$$C + 0.033(760 - P) \tag{9.2}$$

$$F + 0.06(760 - P) \tag{9.3}$$

In these expressions, C and F are the observed flash point temperatures in degrees Celsius and in degrees Fahrenheit, respectively; and K and P are the observed ambient barometric pressures in kilopascals and in millimeters of mercury. The figures 101.3 and 760 will be recognized as the nominal sea level barometric pressures in kilopascals and in millimeters of mercury. A similar correction could be developed for other units of measurement, e.g., for Fahrenheit temperatures with barometric pressures in psia (pounds per square inch absolute). The same flash point correction formulas are used for other flash point methods.

The reported flash point temperatures, after these corrections are applied, are always at the nominal sea level barometric pressure. Thus, the reported flash point temperatures obtained on a substance in a laboratory in Denver (high altitude and low barometric pressure) should be the same (within experimental precision limits) as those obtained by a laboratory at sea level.

In Figure 9.1 and 9.2, the correction (the portion after the + sign in the above corrected values) has been plotted as a function of the observed barometric pressure. The corrections in degrees Celsius for the millimeters of mercury pressure system are shown in Figure 9.1. The correction in degrees Fahrenheit obtained from the pressure in millimeters of mercury is shown in Figure 9.2.

Reading corrections from these graphical plots would be suitable for rough, nonspecification, nonreferee determinations of the sea level flash point temperatures. Use the equations where specifications, government regulations, or other overriding considerations are involved.

BIAS BETWEEN FLASH POINT DETERMINATIONS BY DIFFERENT TEST METHODS

Automated vs. Manual Determinations

In the early 1980s, when automated flash point apparatus became commonplace, there was a concern that the automated and manual versions might yield different results or have different variances. In response to this concern, ASTM S-15 Coordinating Committee on Flash Point conducted three interlaboratory programs to help resolve the matter. The first program compared the automated and manual versions of the Cleveland open-cup device (ASTM Test Method D92); the second program compared the automated and manual versions of the Pensky-Martens closed-cup apparatus (ASTM Test Method D93); the third program dealt with ASTM Test Method D56 of the Tag closed-cup tester [2,3].

ASTM Research Report S15-1009 described the Cleveland open-cup program, in which five of the participating laboratories used manual apparatus and eight used automated apparatus [4]. This interlaboratory program used seven fluids (lubricants and hydraulic fluids of various grades and types) with flash points from about 130°C to about 270°C. The study concluded that there were neither statistically significant differences between the pooled reproducibility variances nor statistically significant biases between the averages of the automated and the manual Cleveland open-cup flash points.

ASTM Research Report S15-1008 described the program using Pensky-Martens manual and automated apparatus [5]. Eleven of the participating laboratories used manual apparatus, and 21 used automated apparatus. The seven samples used in the program ranged from middle distillates to heavier asphaltic materials, with flash points ranging from about 60°C to about 290°C. After rejecting some of the data as outliers, including all the data from two of the higher flash point materials, it was concluded that no significant differences were detected in the reproducibility variances of the automated and manual apparatus. Further, there were no biases detected in the average results with three of the samples, but there were some biases with a light cycle oil and a no. 2 fuel oil sample. In short, we may conclude that, in most cases, the automated versions of D93 (Pensky-Martens apparatus) gave essentially the same results and variances as the manual apparatus.

ASTM Research Report S15-1007 involved Tag closed-cup flash point tester using D56 [6]. Eight samples were used, with 17 laboratories using automated equipment, and 12 laboratories using manual equipment. There was no statistically significant bias between manual and automated Tag closed-cup flash point results.

Details of these studies were published by Montemayor et al. in a paper in the *Journal of Testing and Evaluation* in 2002 [7].

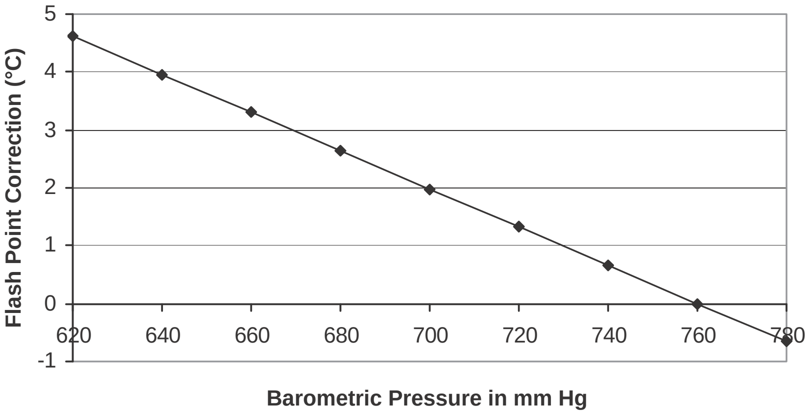

Figure 9.1—Corrections (°C) for atmospheric pressure in mmHg.

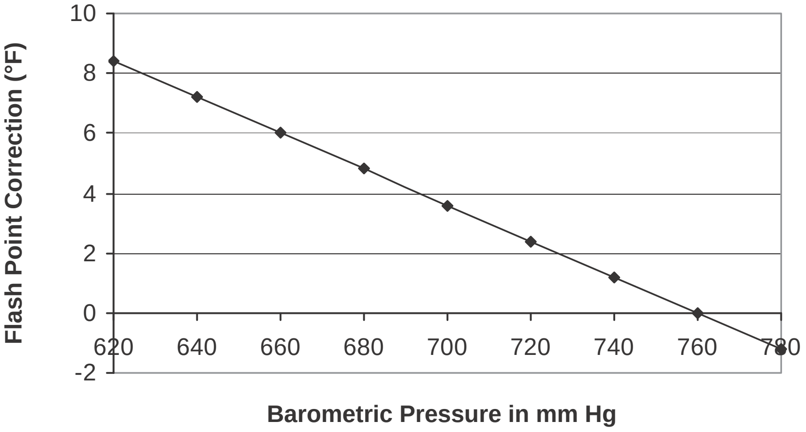

Figure 9.2—Corrections (°F) for atmospheric pressure in mm Hg.

Relative Bias Between Different Test Methods

Different flash point methods may give different values for the flash point. A few ASTM Research Reports and journal articles have addressed this matter. The latest, in June 2004, was ASTM Research Report D02-1581 on the interlaboratory study for ASTM Test Method D7094, the Modified Continuously Closed Cup (MCCCFP) flash point tester [8,9]. The sample set of 16 samples included 7 that were purposely contaminated with a material that was more volatile than the original material. For example, gasoline was added in several concentrations to jet fuels and diesel fuels, biodiesel was added to jet fuel, and diesel fuel was added to lube oil. These were the types of materials that had caused trouble in reproducing ASTM Test Method D93A results when using the original continuously closed-cup (CCCFP) flash point tester according to ASTM Test Method D6450 [10]. Statistical analysis of the data from the interlaboratory program showed no significant bias between the results obtained with the MCCCFP and those obtained with the D93A Pensky-Martens test method for flash points below 150°C.

Turning from the recent to an older attempt at correlating results by different flash point procedures, we find a comparison of the Setaflash apparatus (now called the “small-scale apparatus” in ASTM Committee D01 and D02 standards) with the ASTM Test Method D56 Tag closed-cup apparatus and the Pensky-Martens apparatus in a paper by Harry A. Wray (E. I. du Pont de Nemours and Company, Inc.) in the June 1973 issue of the *Journal of Paint Technology* [11]. The paper notes two studies of flash points determined both by Setaflash and by other standard apparatus:

- An Institute of Petroleum collaborative study involving 13 laboratories was reported by L. H. Bell in 1971 [12]. It was stated that the Setaflash average results were in good agreement with results from the Abel closed-cup, the Tag closed-cup, and the Pensky-Martens closed-cup methods [13].
- At an ASTM Committee D02 meeting in 1972, the results of a comparative study of the Tag closed cup, the Pensky-Martens closed cup, and the Setaflash tester were reported. Using nine samples with flash points ranging from about 80° to about 190°F, the round robin found excellent correlation among the methods with correlation coefficients of 0.9926 for Tag vs. Pensky-Martens, 0.9949 for Setaflash vs. Tag, and 0.9943 for Setaflash vs. Pensky-Martens.

Subsequently, ASTM Committee D01 on Paint and Related Coatings, Materials, and Related Products conducted a comparison study using four paint solvents and five products containing resins and pigments. Although seven laboratories volunteered to participate, the results of only five were used in the statistical analysis of the data because there were insufficient data received from two of the laboratories. The four solvents, all of which had viscosities below 45 SUS (Saybolt Universal Second) at 100° F, were tested using both the Setaflash instrument and ASTM Test Method D56 (the Tag closed-cup method). The five samples contained resins or pigments, and all had viscosities above 45 SUS and/or contained dispersed solids. They were tested using the Setaflash and ASTM Test Method D93 (the Pensky-Martens method).

- The results from the solvents showed identical averages were obtained by both methods with a correlation coefficient of 0.9989 and a regression line equation:

$$\text{FP(Setaflash)} = 0.6474 + 0.9891\ \text{FP(Tag)} \tag{9.4}$$

- The comparison between the Pensky-Martens test method and that of the Setaflash apparatus, using the resins and pigmented products, was said to be slightly poorer than the correlation between the Tag closed cup and the Setaflash. The correlation coefficient was 0.9647, and the regression line equation was:

$$\text{FP (Setaflash)} = 2.6060 + 1.0150\ \text{FP (P-M)} \tag{9.5}$$

EFFECTS OF VISCOSITY, TEMPERATURE RISE RATE, AND STIRRING

Wray, in his paper cited above, also noted some work that showed lower flash points were obtained in testing viscous and/or pigmented samples at the standard temperature rise rate (10°F/min) than at a slower temperature rise rate (3°F/min). The latter rise rate allowed a closer approach to equilibrium conditions. This was given as a partial explanation of the poorer correlation of Setaflash (an equilibrium method and now referred to as small-scale flash point tester) with the Pensky-Martens than with the Tag closed cup.

In the mid-1990s, another study explored these and similar factors. ASTM Committee D02 on Petroleum Products & Lubricants sponsored an interlaboratory program to ascertain the effects of viscosity increases on the flash points measured by ASTM Test Methods Test Methods D93A and D93B (Pensky-Martens), and by the ASTM Test Method D56 (Tag closed cup). Details are provided in ASTM Research Report D02-1350 and a paper by Montemayor in 1999 in the *Journal of Testing and Evaluation* [14,15].

The samples used in this program consisted of high-flash mineral spirits (Varsol 140) to which various concentrations of a long-chain alkyd resin were added to produce mixtures with five different kinematic viscosities ranging from 1.3 mm^2/s (with no alkyd resin) to 50.9 mm^2/s (with 70 % by weight alkyd resin) at 40°C. Eight laboratories participated in the program. Results are shown in Figure 9.3.

It is seen that when flash point determinations by ASTM Test Method D93A were conducted in accordance with the test method instructions with a heating rate of 5°–6°C/min and a stirring rate of 90–120 rpm, the average flash point remained fairly close to 64°C for kinematic viscosity of up to 13.1 mm^2/s at 40°C and then began to decrease, reaching 58.4°C at the maximum viscosity tested (50.9 mm^2/s at 40°C).

In ASTM Test Method D93B, where the heating rate has been decreased to 1°–1.6°C/min and the stirring rate has been increased to about 250 rpm, the flash point remained fairly constant at about 63.5°C up to about a viscosity of 13.1 mm^2/s at 40°C but slightly increased to 65°C at the highest viscosity tested (50.9 mm^2/s at 40°C).

In the third and final evaluation of the effect of viscosities, the interlaboratory program used ASTM Test Method D56, the Tag closed-cup method. When flash points are above 60°C, this method uses a heating rate of about 3°C/min. The apparatus is not equipped with a stirrer, and the sample cup is about 54 mm i.d. (inside diameter), whereas the Pensky-Martens cup is slightly under 51 mm i.d. As seen in Figure 9.3, the flash point was a constant 63.5°C for the two lowest viscosities (1.3 and 1.8 mm^2/s at 40 °C) and then decreases slowly, reaching a low of 61.2°C at the final viscosity of 50.9 mm^2/s at 40°C. In short, the effect of viscosity on Tag flash points was intermediate between the effects on the two Pensky-Martens procedures.

These results raise the question of whether stirring rate or heating rate was the more critical. ASTM Research Report D02-1350 indicated several experiments conducted in 1993 at the Imperial Oil Chemical Division Laboratory. ASTM Test Method D93A was used as the basic method. In one series of experiments, the normal heating rate was reduced to 1.5°C/min; in the other set of experiments, the stirring rate was increased to 250 rpm. In both sets of experiments, the samples were alkyd resin in high-flash mineral spirits, the same combination used in the interlaboratory program. The results are shown in Figure 9.4 as a function of viscosity at 40°C. The results obtained with the standard ASTM Test Method D93A form what appears to be an exponential decay curve with the flash point dropping from about 63.5°C at a kinematic viscosity of

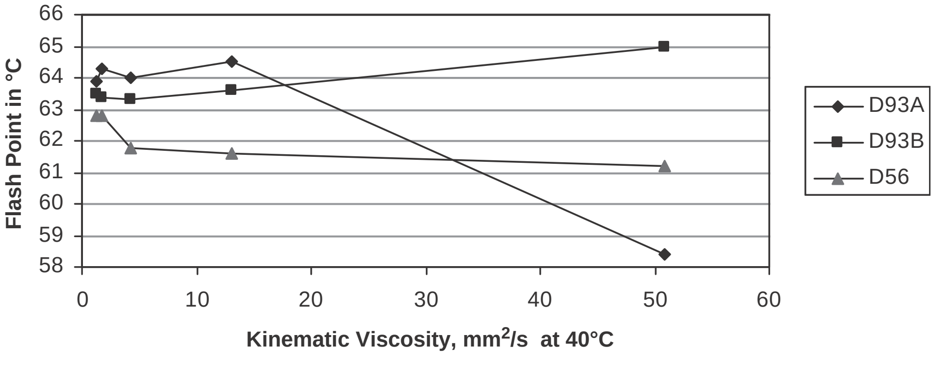

Figure 9.3—Effect of viscosity on flash point measured by Pensky-Martens A and B and by Tag closed cup.

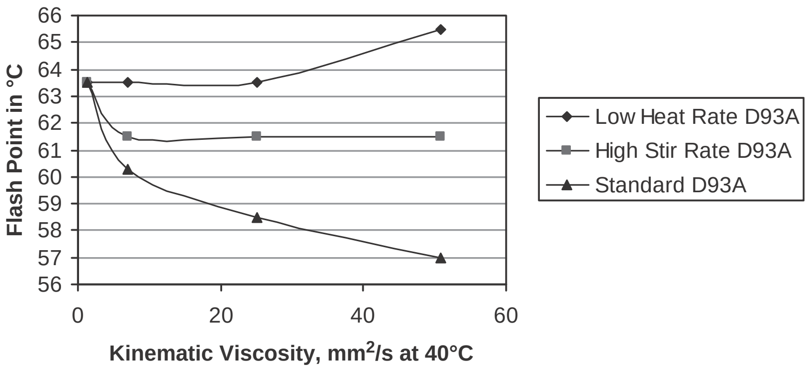

Figure 9.4—The effect of viscosity on the measured Pensky-Martens flash point when high stir rates and low heat rates are used.

1.3 mm^2/s to about 57.0°C by the point where the kinematic viscosity has been increased to about 51 mm^2/s. When the heating rate was reduced, the flash point remained constant at 63.5°C at viscosities from 1.3 to 25 mm^2/s, after which it increased slightly to 65.5°C at a viscosity of about 51 mm^2/s. When the stirring rate was increased to 250 rpm, the flash point dropped slightly from 63.5°C initially at 1.3 mm^2/s to 61.5°C at a viscosity of 7 mm^2/s and remained at that level at the higher viscosities. In short, both low heating rates and high stirring rates alleviate the drop in flash point as viscosities increase.

RELATIONSHIP OF FLASH POINT TO OTHER PROPERTIES

More volatile liquids have lower flash points than less volatile liquids. In the following sections, we explore several flash point relationships. We look at the effects of adding a lower flash point material to a liquid. For example, the effect of minor levels of gasoline contamination in diesel fuels. We also look at the relationship between one of various measures of volatility (the boiling points of pure compounds) and flash point. Finally, we look at the relationship between the distillation curves (simulated) of mixtures (petroleum fuels) and flash point. This subject is, of course, too complex to present a complete picture, but it is hoped this complexity will become evident and the reader will recognize the empirical nature of flash point determinations. Above all, the correlations shown should not be used to estimate a flash point for specification or regulatory purposes where the specific flash point method or methods specified must be used.

Effects of Lower Flash Materials

Several sets of data provided by Rey Montemayor (Imperial Oil Ltd.) serve to illustrate first the effect of the blending of a lower flash point material (undecane) with a higher flash point material (tetradecane) of a similar nature, and second, the effect of contamination of a distillate diesel fuel by lower flash materials (methanol and gasoline).

In the first experiment, undecane (n-C$_{11}$) and tetradecane (n-C$_{14}$) were blended to produce five blends containing 0 %, 25 %, 50 %, 75 %, and 100 % tetradecane by volume. The 100 % undecane had a flash point of 67°C and the 100 % tetradecane had a flash point of 115°C. It was found that the 25 % n-C$_{11}$/75 % nC14 blend had a flash point of 81°C, i.e., 34°C below that of the pure tetradecane, whereas the 75 % n-C$_{11}$/25 % n-C$_{14}$ blend raised the flash point to 70°C, i.e., only 3°C above the flash point of the pure undecane.

In the second experiment, small amounts of gasoline were added to a distillate diesel fuel having a 62°C Pensky-Martens (Procedure A) flash point, to determine the effect of slight contaminations of the diesel fuel with gasoline. As little as 0.1 % (by volume) of gasoline reduced the flash point by 3°C and as little as 0.5 % (by volume) reduced the flash point to below 43°C, almost 20°C below the flash point of the uncontaminated pure diesel fuel.

In the third experiment, the contamination of the same diesel fuel with small amounts of methanol, which may occur from residual methanol during conversion of biodiesel precursors into fatty acid methyl ester (FAME), was examined. It was found that as little as 0.05 % (by volume) methanol reduced the flash point by 6.5°C and as little as 0.2 % (by volume) reduced the flash point to below 43°C, again almost 20°C below that of the pure diesel fuel.

The basic conclusion one reaches from these experiments is that contamination with very small percentages of a substance having a lower flash point can drastically reduce the flash point of the blend below that of the original substance.

Relationship of Flash Point and Boiling Point

One indication of the volatility of a liquid is its boiling point. We would therefore expect the flash point temperature, which is dependent upon a sufficient quantity of vaporized material to support the propagation of a flame, to be some function of the boiling point. On this premise, the author conducted a preliminary study using published values (flash point method used may not be the same) of the flash points and boiling points of a number of alkanes, alkenes, aromatics, and alcohols. The results have been plotted in Figure 9.5, where ● = alkanes; ■ = alkenes; ▲ = aromatics; ♦ = alcohols.

An examination of the plot shows a general linear relationship could exist but that this relationship would be different for each family of organic compound. In fact, a least squares fit for each family separately gives us:

$$\text{Alkanes:}\quad \text{Flash Point} = 0.79(\text{Boiling Point}) - 92 \qquad (9.6)$$

$$\text{Alkanes:}\quad \text{Flash Point} = 0.66(\text{Boiling Point}) - 57 \qquad (9.7)$$

$$\text{Aromatics:}\quad \text{Flash Point} = 0.68(\text{Boiling Point}) - 66 \qquad (9.8)$$

$$\text{Alcohols:}\quad \text{Flash Point} = 0.53(\text{Boiling Point}) - 29 \qquad (9.9)$$

The correlation coefficients were 0.99 for the alkanes, alkenes, and aromatics, and 0.96 for the alcohols.

It will be left to the reader to ascertain whether similar relationships exist between the flash point and such other

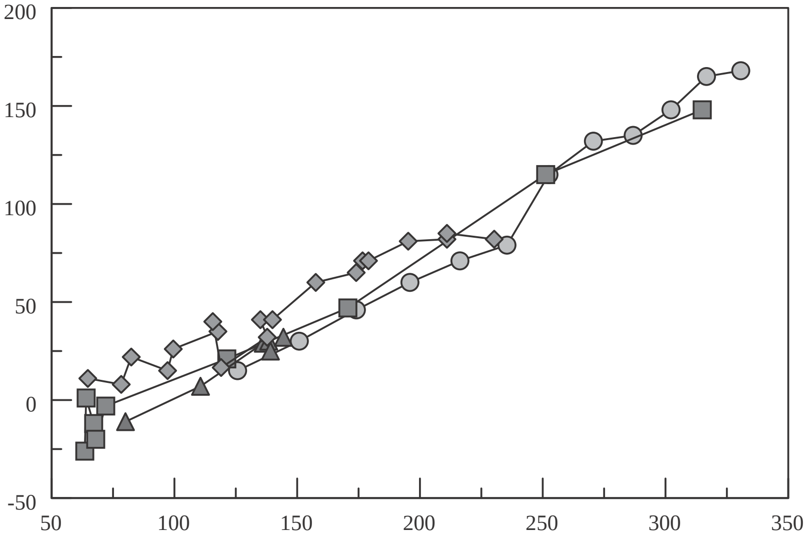

Figure 9.5—Plot of flash point (°C) as a function of the boiling point (°C) (● = alkanes; ■ = alkenes; ▲ = aromatics; ♦ = alcohols).

volatility measures as the vapor pressure at a given temperature and the temperature required for a given vapor pressure.

CALCULATING FLASH POINT FROM SIMULATED DISTILLATIONS

A relatively new test method, ASTM Test Method D7215, which was approved in 2008, allows the calculation of the Pensky-Martens flash point (ASTM Test Method D93) of a distillate diesel fuel and the Tag closed-cup or small-scale flash point (ASTM Test Method D56 or ASTM Test Method D3828) of a jet aviation fuel from data obtained in simulated distillations by ASTM Test Method D2887 using gas chromatography [16–18]. The method is limited to fuels with initial boiling points (IBPs) between 90° and 162°C (194° and 324°F), with a 5 % recovery point temperature (per ASTM Test Method D2887) between 136° and 207°C, and with ASTM Test Method D2887 10 % recovery point temperatures between 142° and 222°C.

ASTM Test Method D2887 simulates distillation by the use of gas chromatography. A nonpolar packed or open tubular (capillary) column is used to elute the components of a hydrocarbon stream in the order of increasing boiling points. Boiling points are assigned to the time axis from a calibration curve using a hydrocarbon mix of known composition.

ASTM Test Method D7215 for Calculated Flash Point from Simulated Distillation Analysis of Distillate Fuels uses the IBP, 5 %, and 10 % points obtained from ASTM Test Method D2887 simulated distillation to obtain calculated flash points (CFP) for the Tag (ASTM Test Method D56), the Pensky-Martens (ASTM Test Method D93), and the small-scale (ASTM Test Method D3828) flash points by the following equations:

$$\mathrm{CFP}_{\mathrm{D}56} = -55.5 + 0.164\mathrm{T}_{\mathrm{IBP}} + 0.095\mathrm{T}_{5\%} + 0.453\mathrm{T}_{10\%} \quad (9.10)$$

$$\mathrm{CFP}_{\mathrm{D}93} = -51.7 + 0.403\mathrm{T}_{\mathrm{IBP}} + 0.163\mathrm{T}_{5\%} + 0.214\mathrm{T}_{10\%} \quad (9.11)$$

$$\mathrm{CFP}_{\mathrm{D}3828} = -61.4 + 0.223\mathrm{T}_{\mathrm{IBP}} + 0.201\mathrm{T}_{5\%} + 0.721\mathrm{T}_{10\%} \quad (9.12)$$

All temperature values are in degrees Celsius. The test method also checks for suitability by setting a mean sum of prediction errors (MSEPX) value of 1.9°C as the maximum permissible.

It seems reasonable to assume that similar relationships could be developed using the results of the various standard distillation procedures, but this has yet to be investigated.

SUMMARY

In this chapter, we have examined a number of flash point relationships and have reached several conclusions:

1. The observed flash point by any of the test methods depends upon the atmospheric pressure (elevation above sea level), but it can be corrected to the equivalent sea level value for any of three equations.
2. There are no statistically significant differences between results obtained with automated flash point apparatus and manual apparatus, and the variances obtained are not statistically different.
3. Although the warning that different flash point test methods may give different results is still applicable, a number of experimental programs have shown that certain test methods give the same statistical results.
4. An increase in the viscosity of a sample tends to lower the flash point obtained with dynamic flash point methods but higher stirring rates or slower temperature heating rates tend to reduce or eliminate this viscosity effect.
5. Contamination with small amounts of a material having a lower flash point can drastically reduce the flash point of the blend below the flash point of the original substance.
6. Flash point tends to be a linear function of the boiling point of pure compounds, but the exact relationship varies with the particular type of compound (alkane, alkene, aromatic, alcohol, etc.).
7. The flash point of a blend of a number of compounds, such as is found in distillate diesel fuels or jet fuels, can be estimated from the initial boiling point and the 5 % and 10 % points obtained in a simulated (gas chromatographic) distillation, but the relationship varies depending upon whether a Tag closed-cup (ASTM Test Method D56), a Pensky-Martens (ASTM Test Method D93), or a small-scale Setaflash (ASTM Test Method D3828) flash point is to be estimated.

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Dr. Montemayor has been the recipient of a number of ASTM International awards including the ASTM International Award of Merit in 2004 for his contribution to standards development in Committee D02. He served on the ASTM Board of Director in 2002-2004

He has authored a number of technical publications related to flash point measurement in the ASTM International Journal of Testing and Evaluation. He was the editor of ASTM MNL 51 *Manual on Distillation and Vapor Pressure Measurement in Petroleum Products* and has written chapters on a number of ASTM publications: MNL 1-7th, MNL 37, and MNL-17th.

Appendix 1

Flash Point Apparatus

SCOPE

Over the years, numerous flash point testers have been designed and used, sometimes for short periods and in only limited geographic areas of the world. The following alphabetical list with brief descriptions or historical references provides information on a number of tester designs. It is based in part on a compilation developed by Dr. David J. Lewis. It is not necessarily a complete listing but does provide a sense of the large number of innovations that have appeared over the years. ASTM, ISO, or other standards currently using the testers are also given when the tester is known to be in current use.

ABEL TESTER

This closed-cup tester, which started as an open-cup design, was developed in August 1876 and adopted by the United Kingdom in 1879 legislation, as a replacement for the Keates tester, for the official testing of petroleum. A stirrer was later added to facilitate the testing of mixtures. The standard oil cup thermometer covers the range from −37° to +82°C (−35° to +180°F).

The Abel Tester is still in use. ISO 13736, however, limits its use to petroleum products and other liquids having flash points between −30° and 70°C, although the precision values given in the test method are only valid for flash points from −5 ° to 66.5°C.

THE ABEL-PENSKY TESTER

This closed-cup tester was developed in Germany in 1879 and adopted as the German standard for testing petroleum in 1882. It incorporates features of the Abel Tester but adds a clockwork timing mechanism to operate the opening of the cover and the flame-dipping sequence, thus aiming to obtain a more strictly controlled testing procedure. The standard thermometer for use in testing oils covers the range 0° to 70°C (32° to 158°F). This apparatus is still used, for example, in the German standard test method DIN 53 213.

ARNABOLDI'S TESTER

This obsolete open-cup tester was similar to, but larger than, the Tag open-cup tester and added a mechanical arrangement for moving the flame of the ignition system over the cup.

BERNSTEIN'S TESTER

This obsolete closed-cup tester was suitable only for flash/no-flash testing. The design was complex. Water was used to expel vapor from a sample cup through an opened tap next to where a test flame was located.

BRAUN'S MODIFICATION OF THE ABEL TESTER

This closed-cup tester, now obsolete, was a German design, which used a magnetic pendulum, arranged to apply the test flame in an Abel tester.

BRENKEN TESTER

This obsolete open-cup tester dates from 1879. A steel crucible was heated in a sand bath held in a larger steel crucible. The smaller crucible contained the sample, and a small test flame was made to approach the sample surface in a vertical direction to test the vapor mixture flammability. The thermometer covered the range of temperatures from 0° to 360°C.

BUREAU OF MINES MODIFIED TESTER

The U.S. Bureau of Mines modified both the basic Pensky-Martens and the basic Abel-Pensky closed-cup testers. The modifications consisted of adapting stirring and slide arrangements from one design to the other and of fitting the oil cups with overflow arrangements for repeatability of sample size. This modified tester is no longer in use.

CLEVELAND OPEN-CUP TESTER (COC)

This tester was in extensive use in the United States by 1908 and is still used today (see ASTM Test Method D92). It uses a brass cup on a heating plate. In early models, a small test flame was moved across the top of the sample cup by hand. However, early in the twentieth century, this was changed to a swinging arm, which controlled the movement of the test flame so that it was at a specified height above the top of the cup. The thermometer for this tester covers the range of temperatures from −6° to +400°C (20°−760°F).

ASTM Test Method D92 states that its primary use is for viscous materials having a flash point above 79°C (175°F) and that it can be used to determine the fire point, i.e., the temperature at which the test specimen will support combustion for a minimum of 5 s. The scope of ASTM Test Method D92 states that the method is applicable to all petroleum products with flash points above 79°C and below 400°C (752°F) except fuel oils.

CONTINUOUSLY CLOSED-CUP TESTER (CCCFP)

Developed around 1990 by Dr. Werner Grabner, this tester is the newest addition to the field of flash point technology and contains a microprocessor that runs the test automatically. Its sample cup holds only 1 or 2 mL of sample. The cup is pressed against a plate that can be either heated or cooled, to form a sample chamber that is closed, but not sealed, during the entire test. The ignition system is an arc that passes between electrodes 2 mm apart. The flash point is detected by the pressure increase in the chamber that results when the flash point is reached. The sample chamber can be regulated for temperatures from −20° to +400°C.

ASTM Test Method D6450, which uses this apparatus, states that the method covers the flash point of fuel oils, lube oils, solvents, and other liquids and that it is suitable for testing samples with a flash point from 10° to 250°C. The method further notes that flash point determinations below the lower of these temperatures and above the higher of the temperatures can be performed but that the precision outside the specified range has not been determined. (U.S. Patent No. 5,176,449; European Patent No. 0 486 980; Japanese Patent No. 2 674 721). ASTM Test Method D7094 uses the same apparatus but different testing parameters.

DANISH TESTER

This obsolete open-cup tester was similar to the Tag open-cup tester but made of copper. Flammability was checked by holding a small flame, e.g., a wooden match, close to, but not touching, the surface of the sample.

ELLIOTT TESTER

This obsolete semiclosed-cup tester, a.k.a. the New York State Closed Tester, was an improved version of the Wisconsin Tester (a glass cover replaced a metallic one). The sample cup (2.75 in. diameter × 4.375 in. high) held on average 316 mL of sample beneath a 1.125-in. vapor space height. A test flame was applied to the surface of the sample.

ENGLER'S ELECTRIC TESTER

This obsolete closed-cup tester used an induction coil to create a spark between platinum points 1 mm apart. The points were located beneath a loosely fitting cover on a closed-cup apparatus that used a glass sample oil cup and had a provision for stirring the sample.

FOSTER AUTOMATIC TESTER

This obsolete semiclosed-cup tester had a small vertical wick with a very small flame in the oil cup. The sample in the cup was heated until a flash in the vapor space extinguished the flame on the wick. The temperature of the sample at that point was taken as the flash point temperature.

GRANIER'S TESTER

This obsolete semiclosed-cup tester used a wick inside the sample cup with the wick projecting 1 mm above the top of a conical section inside the cup. The wick was close to the underside of the cover. When testing for flammability, a small lid built into the cover was removed to apply a test flame. If a slight explosion resulted and if that explosion extinguished the flame, it was deemed a positive result.

GRAY'S TESTER

This obsolete closed-cup tester was originally developed to determine the flash point of heavy mineral oils. In essence, it adapted the slide and stirrer of the Pensky- Martens tester to the Abel tester's sample cup. The stirrer was hand operated through bevel gears that could be disengaged. The same shaft could then be used to actuate the cover opening and the flame tilting movement.

HAASS' MODIFICATION TO VICTOR MEYER'S METHOD

This obsolete closed-cup method fitted the glass cylinder used in the Victor Meyer Method with a hinged copper lid in which there was a small hole. The Victor Meyer Method of heating, shaking, and froth settling was used but, rather than use a flame as in the Victor Meyer Method, a spark was passed between two platinum wires located beneath the lid.

HEUMANN'S MODIFICATION OF ENGLER TESTER

This obsolete closed-cup tester provided a stirrer in the vapor space of the Engler Tester and fitted hinged flaps to the cover of the test cup.

INDIANA STATE TESTER

This open-cup tester is now obsolete. In running the Indiana State test, a lighted taper was allowed to touch the center of the liquid sample.

KEATES' TESTERS

In the United Kingdom, an open-cup tester made by Keates was adopted in 1870 as the official tester under the 1862 Petroleum Act. Because the Keates open-cup test was difficult to run and had poor reproducibility, Abel was asked to address the problem (see Abel's Tester). Keates then proposed his closed-cup tester in 1871 to replace the open-cup design. The two testers are now obsolete.

LETHEBY'S ELECTRIC TESTER

This obsolete closed-cup tester used an electric spark to test the vapor space in a glass cup. The ignition of the vapor-air mixture would blow open a hinged metal cover.

LUCHAIRE OR LUCHAIRE-FINANCES TESTER

Although some references call it a closed-cup tester, it is actually a semiclosed-cup tester because its cover is not completely closed. The apparatus and the associated test method were both developed and are still used in France. However, it is limited to a single use and is being rapidly replaced, with no more instruments being manufactured. A French custom specification for "gazole" refers to the Luchaire method and that is its single use. A working group has developed a bias between the Luchaire and the Pensky-Martens methods, so the latter is the likely replacement.

The sample cup has a stepped design with the portion where the liquid sample resides having a diameter of 63.5 mm and the vapor space above the liquid having a diameter of 78 to 79 mm. The liquid depth may be either 41 mm or 46 mm. The total depth of the cup including the vapor space is 56 mm. The cover to the cup contains a short, open chimney (10-mm diameter × 10 mm high) and two 8-mm diameter holes 120 degrees from the chimney. Any of several thermometers covering different ranges of temperature may be used. Taken together, the thermometers can cover the range from 0° to 420°C. In running the test, a small test flame is positioned just above the chimney. The sample in the cup is heated at a rate of 2° to 3°C per min. The temperature at which the vapors in the cup are ignited by the test flame is taken as the flash point.

MANN'S LAMP APPARATUS

This obsolete apparatus was essentially a metallic lamp in which the wick holder was replaced by a tube closed at the top with a cork. The tube had an opening closed by a flap valve in its side. In operation, the oil to be tested was poured into the lamp. Then the lamp was immersed in a water bath and brought to the test temperature. The slide opening in the tube was then opened and a small flame was introduced to test the flammability of the vapors. Theoretically, when the vapors ignited, the stopper in the end of the tube was intended to be blown out, thus preventing flame from erupting through the side opening.

MARCUSSON TESTER

This obsolete open-cup tester was developed in 1906 and used in Germany for testing lubricating oils and similar substances. In operation, the sample was placed in a glazed porcelain crucible that was heated using a sand bath in a cast iron container. The standard thermometer covered the range from 40° to 410°C.

The test flame was larger than test flames used with other flash point apparatus. The test flame was swung horizontally across the top of the sample crucible, although an early description of the apparatus showed the flame could have an optional downward approach toward the surface of the sample.

MILLSPAUGH'S TESTER

This obsolete closed-cup tester used a glass vessel in which the level of the oil sample was 90 % above the level of the water in a water bath surrounding the vessel. A cover contained two holes with one hole being extended a half inch below the underside of the cover. A cap on the top of this opening would be removed to apply a lighted match to test flammability.

PARRISH'S "NAPHTHOMETER"

This obsolete semiclosed-cup tester incorporated a short tube in the oil cup cover. This tube had a large diameter relative to the size of the cover and contained a lighted wick. When the sample cup was heated, an air current caused the vapor-air mixture from the oil cup to pass into the tube past the lighted wick.

PARRISH-ENGLER "NAPHTHOMETER"

This obsolete semiclosed-cup tester was a modification of the Parrish "Naphthometer." The modification provided control of the air flow through the apparatus.

PEASE'S ELECTRIC TESTER

This obsolete closed-cup tester provided an ignition source by passing an electric spark between wires located in the vapor space.

PENSKY-MARTENS CLOSED-CUP TESTER (PMCC)

This closed-cup tester is still in use (ASTM Test Method D93). It was developed in Germany to test lubricating oils and other materials such as bitumen products whose flash points were well above 100°C. It was based upon the earlier Pensky tester, and its use in Germany dates from about 1870. The apparatus consists of a metallic test cup, a test cover and shutter, a stirring device, a heating source, and an ignition source. The standard thermometer for the unit covers the range from −7° to +370°C (20–700°F).

ASTM Test Method D93 covers petroleum products with flash points from 40° to 360°C. Three somewhat different procedures are incorporated in the test method. Procedure A is applicable to distillate fuels (diesel, kerosine, heating oil, and turbine fuels), new lubricating oils, and other homogeneous petroleum liquids, Procedure B is applicable to residual fuel oils, cutback residua, used lubricating oils, mixtures of petroleum liquids with solids, petroleum liquids that tend to form a surface film, and petroleum liquids of such viscosity that they do not heat uniformly under the conditions of Procedure A, and Procedure C applies to biodiesel fuels.

PENSKY-MARTENS OPEN-CUP MODIFICATION (PMOC)

Shortly after the use of the Pensky-Martens closed-cup tester was initiated, it was found that it could also be used as an open-cup tester by removing the cover assembly and testing the vapors over the surface of the sample. Consequently, the cover was replaced with an assembly to hold the thermometer at the desired angle and to position a small test flame over the center of the cup. The Institute of Petroleum promulgated Standard IP35 using this configuration in 1935 with a range of application that is the same as that for the closed-cup system.

RAPID EQUILIBRIUM TESTERS

See the Small-Scale (Setaflash) Testers.

RUSSIAN VNIIPO TESTER

This obsolete open-cup tester was in use prior to 1958. The porcelain test cup, flat bottomed and conical in shape, was placed on an asbestos bottom liner inside a conical recess in a steel heating unit. A small test flame was moved across the top of the cup by hand. Thermometers used with the tester covered the range from −30° to +300°C and were supported by a stand designed so the thermometer could be swung away from the cup if the sample caught fire. A special cover was then placed over the cup to extinguish the flame.

SALLERON-URBAIN APPARATUS

This obsolete apparatus was not a flash point tester; rather, it obtained the vapor pressure of the sample at 15°C. An estimated flash point temperature was then calculated based on the vapor pressure.

SAYBOLT'S ELECTRIC TESTER

In this obsolete open-cup tester, ignition was initiated by the discharge of an induction coil between platinum points that were placed a fixed distance above the surface of the sample.

SMALL-SCALE (SETAFLASH) TESTERS

These closed-cup testers were invented by T. Kidd (Esso Petroleum) in the early 1960s. They were first marketed in various versions by Stanhope-Seta Ltd. between 1967 and 1969 to cover testing ranges from −40° to +300°C. They use a much smaller test specimen than most other flash point testers, so they are referred to as rapid equilibrium testers, as "small scale closed-cup apparatus" (ASTM Test Method D3278), and as "small scale closed testers" (ASTM Test Method D3828). IP standard 303 is comparable to ASTM Test Method D3828. An open-cup version is also available, the "small scale open-cup apparatus" of ASTM Test Method D4206, although, in this case, the test method is for testing the ability of a material to support combustion rather than for determining the flash point. ASTM Test Method D7236 essentially uses the same apparatus but different testing parameters.

The basic commercial tester uses an electrically heated metal block (62 mm diameter × 36.5 mm high). The metal is aluminum alloy or other high thermal conductivity metal. For a closed-cup apparatus, a 9.9-mm depression is made in the top of the block. For an open-cup apparatus, the depression is either 6.3 or 9.5 mm deep. The metal block is mounted in an electrical heating/cooling unit equipped with a temperature sensor. The heat flow to the block is controlled electronically to raise the block's temperature to a "set" value.

In conducting a test, a small test specimen (either 2 mL or 4 mL, depending on the specific configuration of the apparatus) is injected into the cup. This results in a liquid depth of 1.0 or 2.1 mm in closed-cup tests and 4.8 in. in open-cup testing. After a timed delay of 1 or 2 min, a test flame is applied. A fresh test specimen must be used after each test flame application. When a positive flash is obtained, the metal block temperature is taken as the flash point temperature.

SQUIRE'S TESTER

This obsolete open-cup tester used an arrangement similar to that of the Cleveland open-cup tester. However, in testing, the temperature was allowed to stabilize by removing the heat source before the test flame was applied.

TAG CLOSED TESTER (TAG OR TCC)

This closed-cup tester based on Tagliabue's design was developed and tried in 1916 following trials of available flash point testers in 1914–1915. ASTM subjected it to a full comparison series of tests in 1917. The original design of the apparatus, i.e., the use of soft solder in the cup and cover, limited its range to −7° to +93°C (20° to 200°F).

ASTM Test Method D56, which uses this apparatus, is intended for use with liquids having a viscosity below 5.5 mm^2/s at 40°C or below 9.5 mm^2/s at 25°C and a flash point below 93° C. The test method has been adopted by U.S. government agencies to replace several Federal Test Methods.

TAG OPEN-CUP TESTER (TOC)

The modern Tag open-cup tester (ASTM Test methods D1310 and STM D3143) is derived from the Tagliabue open-cup tester patented in 1862. The ASTM studies of 1914 showed that cups being used varied in size from 67 to 100 mL. Therefore, tests were conducted in 1915 using carefully standardized glass and brass cups. Two methods of flame application were used in those tests: (1) a horizontal sweep over the cup, and (2) a vertical approach to 1/8 in. above the surface of the liquid test specimen. Although a guide was provided for the horizontal sweep, no official standard was prepared at that time. A swinging arm standard for the test flame was standardized in 1952 when ASTM Test Methods D1310 was first issued.

The modern, standardized Tag open-cup tester uses a glass test cup surrounded by a water bath heating system. The standard thermometers cover the range from −38° to +163°C (−36° to +325°F). ASTM Test Method D1310 covers the determination of flash points and fire points of liquids having flash points between 0° and 325°F (−18° and 165°C).

TAGLIABUE'S LARGE CLOSED TESTER

This obsolete semiclosed-cup tester was similar to Tagliabue's Original Small Closed Tester, but it used a glass rather than a metallic cup and was larger overall.

TAGLIABUE'S ORIGINAL SMALL CLOSED TESTER

Despite its name, this obsolete tester was actually a semiclosed-cup tester. It was one of the first testers invented (about 1860). The metallic test cup (50 mm diameter × 25 mm deep) was fitted with a cover having a short chimney. This cover was equipped with valves to let air in and to cause vapor to rise into the chimney where a flame was applied. This tester was sometimes called a "coal-oil pyrometer."

VICTOR MEYER'S INSTRUMENT

This obsolete closed-cup tester used a corked cylinder in which a test specimen was heated to a specified temperature in a water bath. When the desired temperature was reached, the cylinder was removed and shaken, then allowed to stand quiescent until any froth had broken. At that time, the cylinder was uncorked and a small test flame was applied to the top of the cylinder.

WISCONSIN TESTER

This obsolete semiclosed-cup tester used a copper test specimen cup with a copper cover provided with a small opening through which the test flame was inserted.

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