

## MEASUREMENT OF FLASH POINTS: APPARATUS, METHODOLOGY, APPLICATIONS

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### Summary

The flash point provides a simple, convenient index for the flammability of diverse materials. In this paper, flash point apparatus and methodology are surveyed and some applications highlighted, including use in the study of spill control agents for flammable solvents. The reliability of the Setaflash closed tester is confirmed. The formulation and use of liquid mixtures to assure the performance of flash point testers is described.

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For the assessment of the flammability of diverse samples, determination of the flash point is the simplest, fastest, and most used approach. Flash point measurements were introduced in England as early as 1862 for the control of the quality of kerosene for lamps [1]. The flash point tester designed by Keates was officially adopted in England in 1870. A decade later, the Abel design was introduced in Germany and was soon modified by Pensky. The Abel-Pensky instrument and that designed by Tagliabue in the same period are directly related to modern flash point testers.

In the latest definition being considered by the ASTM, the flash point is "the lowest temperature, corrected to a pressure of 101.3 kPa (1013 mbar) at which the application of an ignition source causes the vapors above the sample to ignite, under the specified conditions of test" [2]. This definition, while descriptive, does not relate the flash point to other physical properties. The flash point is related directly to the boiling point and inversely to the vapor pressure at a given temperature. Flammable liquids with a high vapor pressure at "normal" temperatures commonly exhibit a low boiling point and a low flash point.

The physico-chemical significance of the flash point was considered by Ormandy and Craven in 1923, and for pure liquids the vapor pressure was correlated with the flash point [3]. Goto and Nikki have delineated the relationship between vapor pressure, heat of vaporization, and flash point for certain classes of aromatic compounds [4]. The relation between boiling point and flash point within a homologous series was considered by Akmetzhanov and coworkers [5]. For normal alkanes and carboxylic acids, the relationship was found to be linear. Over the past 6 years, Wiswesser has

accumulated data for several thousand liquid organic compounds [6]. For most homologous series, the relationship between vapor pressure or boiling point and flash point is essentially linear.

### Types of flash point testers

Flash point testers can be divided into two descriptive types: Open cup and closed cup (see Fig. 1). In the open cup technique, the sample is heated

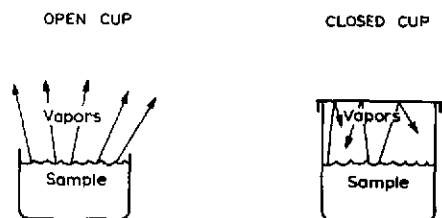


Fig. 1. Conditions in open cup vs. closed cup flash point testers.

in an open vessel to a selected temperature. A test flame (or other ignition source) is introduced over the surface of the sample and it is noted whether ignition occurs. If not, the temperature is raised and the process repeated until flashing occurs. The open cup tester approximates conditions that are met in open vessels and that would be encountered in spills. One disadvantage of open testers is that low boiling components of the sample mixture may be lost to the atmosphere prior to the application of the flame; consequently, a high flash point value may be obtained that is not representative of the sample. In the closed cup technique, the sample is separated from the surrounding atmosphere by a physical barrier, preventing the loss of low boiling components. Additionally, an equilibrium is approximated between the vapor of the sample and the air in the enclosed space, provided the rate of temperature increase is small. At a selected temperature, the barrier is removed, an ignition source is introduced, and it is noted whether flashing occurs. If not, the temperature is raised and the process repeated until flashing is observed. The closed cup technique allows an insight into the flammability of the sample within an enclosed space such as a sealed container.

### Parameters affecting flash point values

In view of the importance of the flash point in assessing flammability, it is unfortunate that the values secured can be decidedly dependent on the technique and instrument used. Some of the parameters that affect flash point values can be briefly considered.

They are: Tester configuration; Sample size; Ignition source; Temperature control; Ambient pressure; Sample homogeneity; Drafts; and Operator bias.

The flash point value may differ from one type of tester design to another,

especially if the dimensional ratios and configurations are different. Care should be taken to assure that the recommended size of the sample is placed in the tester because the volume of the air space above the sample surface can influence the flash point value. In modern commercial instruments, the ignition source is a small test flame, which should be regulated to the size indicated by a template provided with the instrument. If the flame is too large, erroneously low flash point values can be secured. The temperature increment and the rate of temperature increase should be carefully selected, as the thermal lag will be influenced. The recommended rate of temperature increase near the expected flash point is  $2^{\circ}\text{F}$  per minute for most testers.

Factors external to the tester can also influence the flash point value. The flash point is dependent on the ambient pressure, and for reporting should be corrected to standard barometric pressure (that is, 101.3 kPa, 1013 mbar, or 760 mm of Hg). The correction commonly applied is the addition or subtraction of  $0.06^{\circ}\text{F}$  to the found value for each millimeter of mercury below or above 760 mm, respectively. Drafts over and around the tester can alter heat loss from the unit, thereby affecting the values secured. In securing a representative sample of a material, special precautions may be required. Homogeneity of the material must be established before sampling, and the sample must be maintained tightly capped to prevent the loss of low-boiling components and be made homogeneous before transfer to the test cup.

Operator bias can take various forms and bad habits, once established, may be hard to eliminate! All operators should be trained fully and similarly on the same type of instrument. In our laboratories, flash point values for a sample secured on a single instrument by two well-trained operators usually agree within  $1^{\circ}\text{F}$ , within the range  $40^{\circ}$ – $150^{\circ}\text{F}$ . However, differences as much as  $5^{\circ}\text{F}$  have been obtained where performance has been sloppy.

### Modern flash point testers

The measurement of flash point is somewhat more complicated than might be hoped for, and it is not always easy to secure reliable, reproducible values. Consequently, there has been a continuing effort to standardize both instruments and procedures for their use. In the United States, the American Society for Testing Materials (ASTM) has been active for many years. Table 1 summarizes the flash point testers for which the ASTM currently provides criteria and methods.

The Tag closed tester (Fig. 2) is commonly used for determining the flash points of mobile liquids flashing below  $200^{\circ}\text{F}$ . This tester, with ASTM method D56, has been adopted by the U.S. Department of Transportation (DOT) for the regulatory classification of flammable and combustible liquids, and is widely used in the varnish and lacquer industries and by firms supplying petroleum-based solvents.

The Tag open-cup tester (Fig. 3) can be used for a variety of liquids exhibiting flash points below  $325^{\circ}\text{F}$ . Since the adoption by the DOT of closed

TABLE 1

Some flash point testers approved by ASTM (1976) [7]

Name	Designation	Samples covered*
Tag closed tester	ASTM D56	Mobile liquids flashing below 200°F (93.3°C)
Tag open-cup tester	ASTM D1310	As above, including paints and asphalts
Pensky—Martens closed tester	ASTM D93	Liquids and suspensions flashing below 700°F (369°C)
Cleveland open-cup tester	ASTM D92	Liquids and suspensions flashing from 175–760°F (77–445°C)
Setaflash closed tester	ASTM D3278	Mobile liquids flashing below 230°F (110°C)

\*The viscosity of the sample can determine which tester is used; see the designated ASTM procedure.

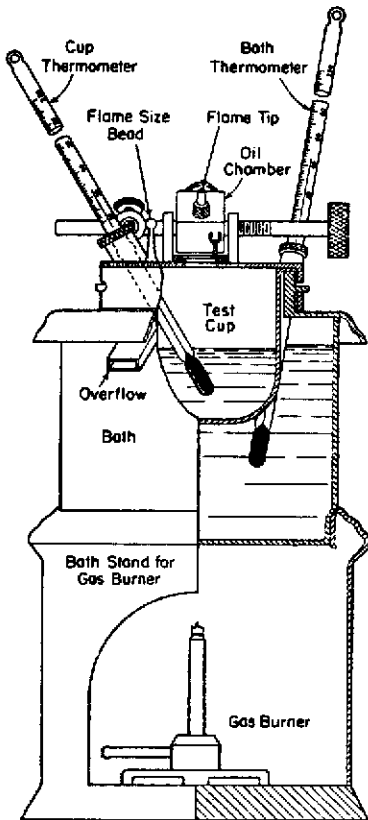


Fig. 2. Tag closed tester [7].

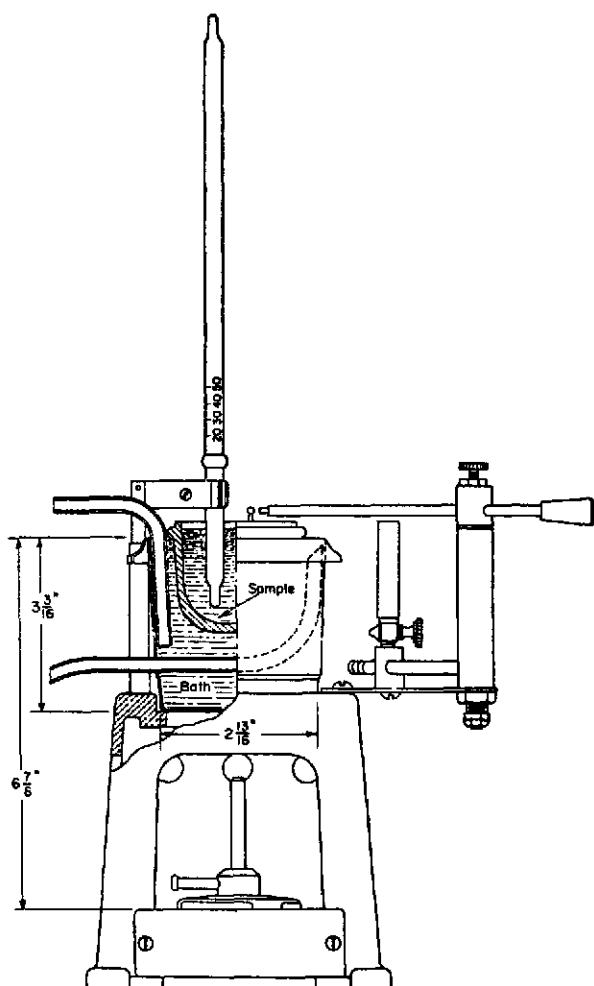


Fig. 3. Tag open-cup tester [7].

cup methods for regulatory purposes, this tester is largely used for special samples, especially in the paint and varnish industry.

The Pensky-Martens closed tester (Fig. 4) is used mainly for the assessment of fuel and lube oils, suspensions, and solvent-type waxes. It is provided with a stirrer, and is thereby favored for determining the flash point of viscous liquids. It can also be used to detect minor amounts of volatiles in, for example, lube oils.

The Cleveland open cup tester (Fig. 5) is used in some industries to determine the flash point of viscous liquids and petroleum products that flash above 175° F. Low-boiling volatiles can also be detected with this instrument.

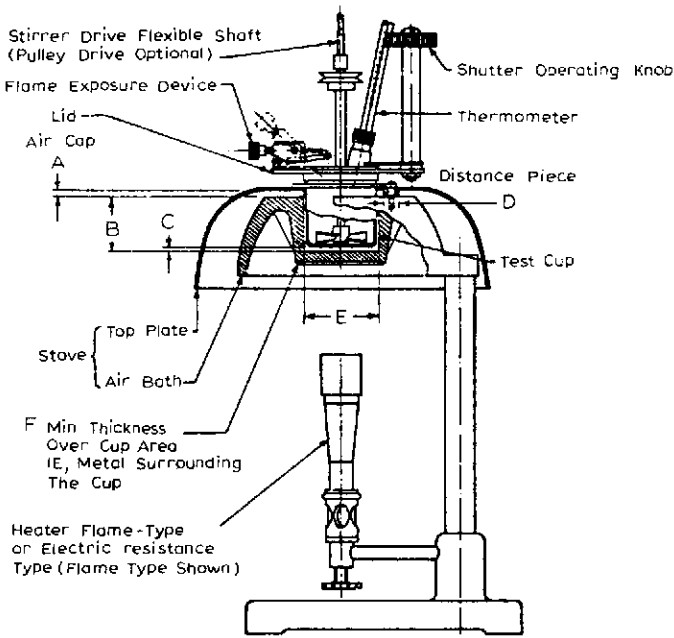


Fig. 4. Pensky—Martens closed tester [7].

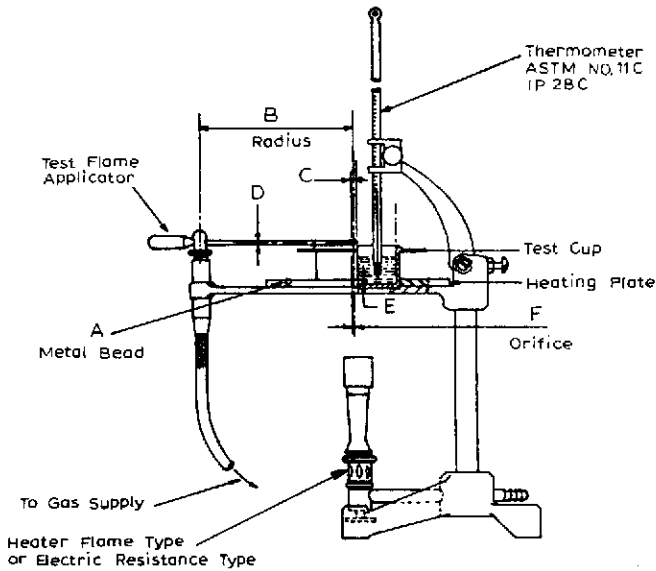


Fig. 5. Cleveland open-cup tester [7].

In the early 1960's, M.T. Kidd of Esso Petroleum in England developed a tester that has been perfected by Stanhope—Seta Ltd. [8]. This tester, known as the Setaflash<sup>®</sup> closed tester (Fig. 6), allows the rapid assessment of flash points below 230° F. A modified high temperature model from the same firm allows flash points up to 572° F to be rapidly assessed.

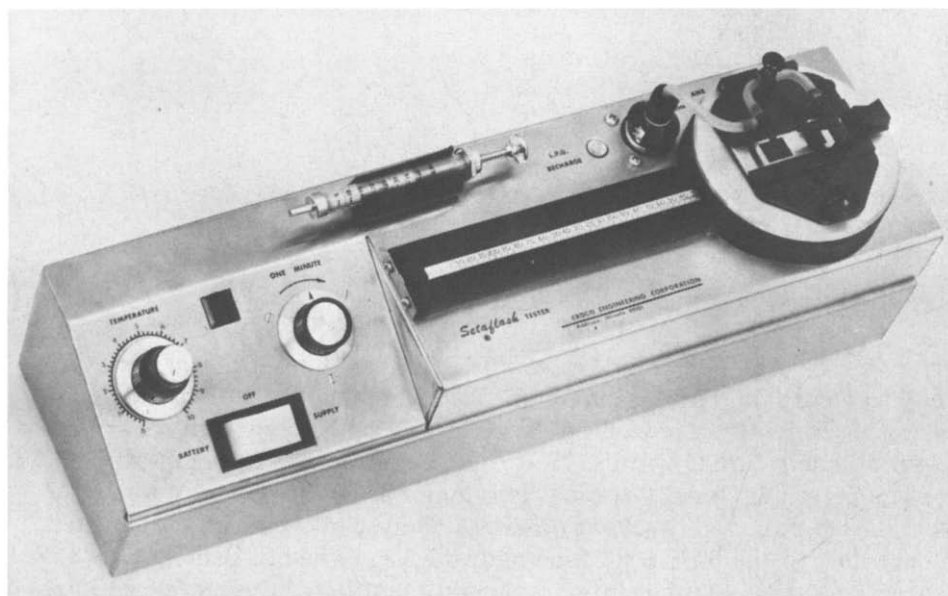


Fig. 6. Setaflash closed tester.

### Setaflash tester performance and advantages

In 1973, Wray reported ASTM round-robin findings comparing Setaflash and Tag closed testers [9]. Initial studies of the ASTM D-2 Committee indicated excellent agreement between the two testers. An extended study by the ASTM D-1 Committee with 4 liquid samples run by 5 or more laboratories confirmed this agreement. The D-1 data are summarized in Table 2 (corrected for errors in original article [9]).

The average value for each sample by the two testers were in excellent agreement. The standard deviation secured within a single laboratory (that is, the repeatability) was about 1° F for the Setaflash and about 1.2° F for the Tag unit. The standard deviation for the pooled data (reproducibility) was about 1.5° F and 1.7° F for the two testers, respectively.

As a result of the studies of these ASTM committees, and the subsequent efforts of the ASTM Ad Hoc Committee on Flash Point Testing and Government Response, the Setaflash closed tester was adopted by the DOT in 1976 as the alternative to the Tag closed tester for the flammability clas-

TABLE 2

Comparison of flash points from Tag and Setaflash closed testers performance, ASTM D-1 round-robin [9]

Sample	Setaflash	Tag
	<i>Average flash point, (°F*)</i>	
A	43.35	43.80
B	78.10	78.78
C	105.05	106.20
D	182.95	185.20
	<i>Standard deviation</i>	
Repeatability	0.9843	1.1885
Reproducibility	1.5483	1.7446

\*Average of duplicates from 5 contributing laboratories.

sification of mobile organic liquids [10]. Before this adoption it was necessary to secure the flash point via the Tag closed tester. During that period, many flash points were secured in our laboratories using both testers, the results usually agreed within 1°F for liquids flashing in the range 40–150°F.

The Setaflash closed tester has two major advantages: use of a small sample and cup, and excellent precision. Only 2 ml of sample is required, in contrast to the 50–70 ml used with the Tag closed or Pensky–Martens units. This small volume allows rapid equilibration of the sample and its vapors with the enclosed air. The small cup assures rapid thermal equilibrium and reduces thermal lag. As the ASTM data in Table 2 indicate, replicate flash points secured on the Setaflash tester are in better agreement than for the Tag unit. With the Setaflash unit, in our laboratory a standard deviation of 1°F is commonly obtained by a single well-trained operator. Often the standard deviation approaches 0.5°F, which may be the ultimate precision attainable because thermometer readings cannot be estimated to better than 0.5°F. This tester may be used either in a flash/no flash mode for specification flash point testing or for the determination of actual flash points. The Setaflash tester is specified to be used under equilibrium conditions rather than at a specified rate of heating as for the other methods listed in Table 1. This is considered to be a factor in its superior performance.

### Classification of flammable and combustible liquids

On January 1, 1977, DOT regulations for the classification of flammable liquids became effective that stipulate that the closed cup flash point is the sole criterion for classifying a liquid as “flammable” or “combustible” [11]. The DOT flammability classification scheme is delineated in Table 3.

In brief, a substance is classified by the DOT as “flammable” if the flash point is below 100°F (37.8°C) and as “combustible” if the flash point lies



TABLE 3

## Flammability classification of liquids

DOT Class	DOL Class	Flash point range
Flammable		< 100°F (< 37.8°C)
Flammable	Flammable IA	< 73°F (< 23°C) (boiling point < 100°F)
Flammable	Flammable IB	< 73°F (boiling point ≥ 100°F)
Flammable	Flammable IC	≥ 73°F and < 100°F
Combustible		≥ 100°F and < 200°F (93.3°C)
Combustible	Combustible II	≥ 100°F and < 140°F (60°C)
Combustible	Combustible IIIA	≥ 140°F and < 200°F
Combustible	Combustible IIIB	≥ 200°F

between 100 and 200°F (93.3°C). The U.S. Department of Labor (DOL) categories for the storage of flammable liquids are also indicated in Table 3 [12].

Since the DOT regulations hold a manufacturer responsible for flash point values appearing on labels, the manufacturer should determine the flash points for his relevant products using an approved tester, and not rely on literature values.

#### Calibration liquids for flash point testers

Materials for flash point calibration liquids must exhibit the following criteria:

- Flash Points bracket desired value
- Similar vapor pressure (or boiling pt.)
- Similar molecular weight
- Similar structure
- Similar functionality
- No decrease in flash point on partial evaporation

For checking the condition and operation of the Tag and Setaflash closed testers, the ASTM has specified *p*-xylene. Recently the ASTM Ad Hoc Committee has noted that *p*-xylene can exhibit flash point values over a wider range than specified [14]. This committee currently has underway a round-robin study of six different organic liquids of reagent grade quality as possible calibration liquids covering the range from 0°F to 300°F.

In our laboratories, we are approaching flash point calibration from a different viewpoint. For product classification, it is important that the user of a flash point tester be assured that his instrument is operating reliably at or near the specified temperatures (see Table 3). We considered preparation of a set of liquids that would exhibit flash points close to the specified temperatures. However, it is difficult to secure common compounds having suitable flash points. Additionally, because of the difference in purity from lot-to-lot, the flash point could vary significantly. We then hit on the idea

of mixing two or more miscible liquids and adjusting their ratios empirically to attain the exact flash point value desired [15]. For practical purposes the prepared mixture should not, on partial evaporation, exhibit a significant change in the flash point value.

The approach used is to choose two or more stable liquids with flash points bracketing the desired value and that additionally exhibit similar molecular weight, functionality, structure, and vapor pressure (or boiling point). This approach can be delineated in terms of the preparation of a calibration liquid to flash at 100°F. Cumene and pseudo-cumene were selected as the two components. The physical properties of the two compounds are given in Table 4.

TABLE 4

Physical properties of cumene and pseudo-cumene

Parameter	Cumene	Pseudo-cumene
IUPAC name	Isopropylbenzene	1, 2, 4-Trimethylbenzene
Functionality	Alkylbenzene	Alkylbenzene
Molecular weight	120.20	120.20
Boiling point	152°C	169°C
Vapor pressure	10 mm/38°C	10 mm/35°C
Flash point (Setaflash)	88°F	117°F

The flash point of a selected lot of each of these alkylbenzenes was established with an optimized Setaflash tester by replicate measurements with a thermometer compared with an NBS calibrated thermometer. As shown in Fig. 7, these values were plotted as a flash point versus composition graph, and a straight line drawn through the two points. The composition of a mixture expected to yield a flash point of 100°F was then estimated. Then, two mixtures bracketing the desired composition were prepared and

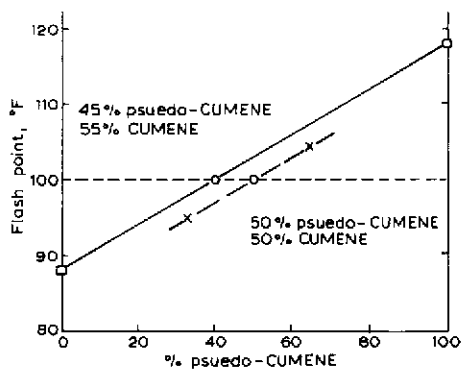


Fig. 7. Graphic estimation of cumene:pseudo-cumene ratio to produce 100°F flash point calibration liquid.

their flash points established. These values were plotted on a graph. A straight line was drawn through these points, and the composition flashing at 100°F was read. A large volume of this composition was then prepared from the selected lots of starting materials. The resulting mixture exhibited an average flash of 100°F with a standard deviation of 1°F (nine determinations). The series of linear approximations can, of course, be followed either algebraically or by simple proportion. The number of approximations needed depends on the compounds involved and may be reduced for the production of subsequent batches of a given calibration liquid.

Using this technique, we have prepared flash point calibration liquids exhibiting flash point values of 73°F, 100°F, 120°F, and 200°F. In all cases, the flash point values were within 1°F of the desired value, as determined by replicate measurement on the Setaflash instrument. It may be added that the flash point values secured for these mixtures with Setaflash and Tag closed testers were in good agreement ( $\sim 1^\circ\text{F}$ ).

Each of the four calibration liquids was allowed to remain in open dishes at room temperature for up to 2 days, until a significant (10–50%) portion had evaporated. In all cases, the flash point of the remaining liquid was within 2°F of the original mixture.

### Types of samples assessed by flash point

From its introduction over a century ago, the principal use of flash point measurements has been in the assessment of the flammability of mobile liquids. The technique has been extended to diverse samples such as viscous liquids (oils, cut-back asphalts), suspensions of solids (paints, pigmented varnishes), and materials forming surface films.

Wright in 1922 used the flash point to determine the molecular weight of organic compounds [16]. Wright's approach has apparently not been pursued by later workers. It is noteworthy, however, that he designed a tester, somewhat complex and not for routine use, that was reported to exhibit a reliability of 0.05°C.

In our laboratories, flash point measurements have been of recent value in the development and assessment of agents for the treatment and cleanup of solvent spills. Some of the findings have been reported [17]. For laboratory spills, the agent of choice should not only absorb or otherwise immobilize a flammable solvent, but should reduce the flammability. The Setaflash closed tester has proved especially useful in this research. Only a 3-gram sample of the solvent-treatment agent mixture is required for the determination of the flash point. For a given mixture, the flash point is usually reproducible to 1°F. Using this technique, the relative reduction of the flammability hazard of representative solvents with various treatment agents can be assessed, and the appropriate treatment ratio can be estimated. Table 5 presents typical findings for toluene and various treatment agents.

The best overall results were obtained using Solusorb<sup>TM</sup>, a proprietary

TABLE 5

Elevation of the flash point of toluene using various treatment agents\*

Treatment agent	Flash point (°F)**
Diatomaceous earth	41
Perlite	42
Sand	46
Silica gel, activated (60—200 mesh)	68
Alumina, Brockman I, activated	78
Solusorb™	≥ 230

\*Using a 10:1 agent: solvent applications ratio. \*\*Flash point of toluene alone is 42°F.

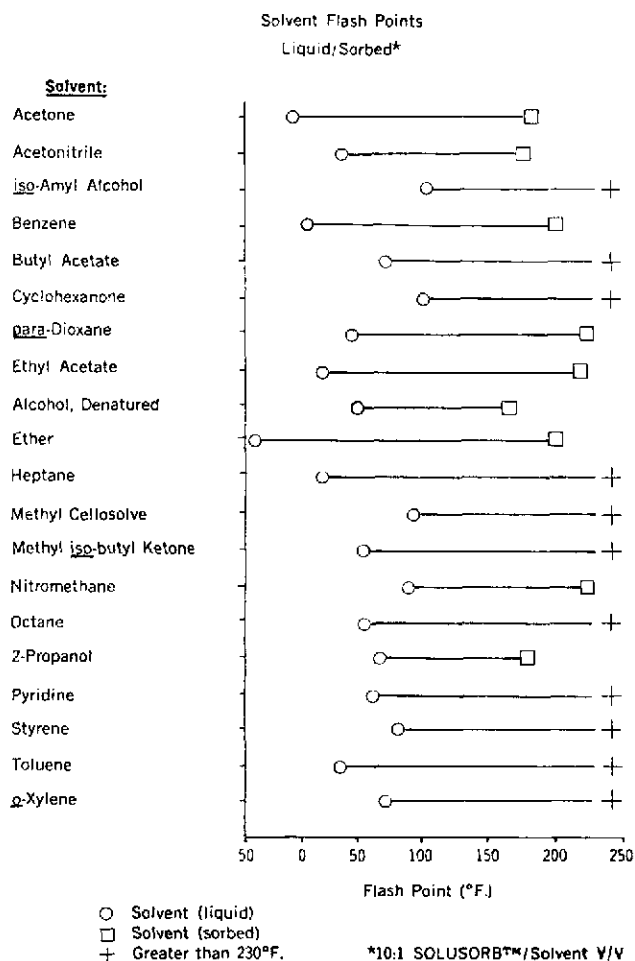


Fig. 8. Elevation of the flash point of common solvents by sorption on Solusorb™ [18].

active absorbant now offered by J.T. Baker Chemical Company for the clean-up of laboratory spills of flammable solvents [18]. Fig. 8 highlights the elevation of the flash point of common solvents when Solusorb<sup>TM</sup> is applied at a 10:1 absorbent:solvent ratio.

It will be seen that in all cases the flash point of the treatment mixture is 50°F or more higher than that of the untreated solvent. It is noteworthy that many of the treated solvents do not burn even when a match is applied directly to the surface of the mixture. Even when burning occurs, it is controlled, with very slow flame spread; indeed, the flame can be extinguished by covering it with surrounding or added absorbent.

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