

Safety Research Center
Report No. S4131
Auth. No. 8836
April 29, 1970

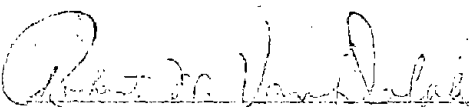
PB193077

RECOMMENDATION OF FLASH POINT METHOD FOR EVALUATION OF
FLAMMABILITY HAZARD IN THE TRANSPORTATION OF FLAMMABLE LIQUIDS

By

Joseph M. Kuchta
David Burgess

APPROVED:


Robert W. Van Dolah
Acting Research Director
Safety Research Center

Reproduced by
**NATIONAL TECHNICAL
INFORMATION SERVICE**
Springfield, Va. 22151

N O T I C E

THIS DOCUMENT HAS BEEN REPRODUCED FROM THE
BEST COPY FURNISHED US BY THE SPONSORING
AGENCY. ALTHOUGH IT IS RECOGNIZED THAT CER-
TAIN PORTIONS ARE ILLEGIBLE, IT IS BEING RE-
LEASED IN THE INTEREST OF MAKING AVAILABLE
AS MUCH INFORMATION AS POSSIBLE.

STANDARD TITLE PAGE FOR TECHNICAL REPORTS	1. Report No. USBM-S4131	2. Govt. Accession No.	3. Recipient's Catalog No.
4. Title and Subtitle "Recommendation of Flash Point Method for Evaluation of Flammability Hazard in the Transportation of Flammable Liquids"		5. Report Date April 29, 1970	6. Performing Organization Code
7. Author(s) Joseph M. Kuchta and David Burgess		8. Performing Organization Rept. No. S4131	
9. Performing Organization Name and Address Safety Research Center U. S. Bureau of Mines 4800 Forbes Avenue Pittsburgh, Pennsylvania 15213		10. Project/Task/Work Unit No.	
		11. Contract/Grant No. DOT-OS-00007	
12. Sponsoring Agency Name and Address Office of Hazardous Materials Department of Transportation Washington, D. C. 20590		13. Type of Report & Period Covered Final	
		14. Sponsoring Agency Code	
15. Supplementary Notes Report No. S4131A, "Additional Evidence in Support of the Closed Cup Flash Point Method", is incorporated as an integral part of Report No. S4131.			
16. Abstracts This report consists of recommendations, with supporting data and reasoning, for use of the Tagliabue (Tag) Closed Cup Method to determine the flash points of flammable liquids for transportation hazard classification purposes. It presents comparative data for Tag open cup and Tag closed cup flash points and for Tag closed cup values and those calculated from lower flammable limits. It compares repeatability and reproducibility of several types of testers. The behavior of mixtures is treated along with that of neat liquids. The report does not include a separate bibliography, but does cite a number of significant references.			
17. Key Words and Document Analysis. 17a. Descriptors 1,2Combustion, combustibility, combustible liquid, 3,4ethyl acetate, flammability limit, flammability testing, flammable liquids, flammable zone, Halon 233, hazard, n-heptane, hydrazine, ignition, isopropanol, JET A, JP-4, methanol methyl ethyl ketone, 2-nitropropane, safety, solvents (a number of individual ones shown), toluene, unsymmetrical dimethylhydrazine, vapor pressure, xylene. 1n-butanol 2n-butyl acetate 3dimethyl formamide 4dimethyl sulfoxide			
17b. Identifiers/Open-Ended Terms Hazardous materials transportation; Cleveland Open Cup Method; Tagliabue Closed Cup Method; Pensky-Martens Method; vapor pressure vs. temperature. <u>Solvents, cleaners, and abrasives; laboratories, test facilities,</u> <u>and test equipment; general concepts; combustion and ignition.</u>			
17c. COSATI Field/Group			
18. Distribution Statement This is to be made available to the general public with no limitations.		19. Security Class (This Report) UNCLASSIFIED	21. No. of Pages
		20. Security Class (This Page) UNCLASSIFIED	22. Price



UNITED STATES
DEPARTMENT OF THE INTERIOR
BUREAU OF MINES

4800 FORBES AVENUE
PITTSBURGH, PENNSYLVANIA 15213

Safety Research Center

RECOMMENDATION OF FLASH POINT METHOD FOR EVALUATION OF FLAMMABILITY
HAZARD IN THE TRANSPORTATION OF FLAMMABLE LIQUIDS

INTRODUCTION

The flammability hazard in the transportation of combustible liquids is partly defined by the temperature at which flammable vapor-air mixtures can be formed. The flash point of a liquid in air is useful in this connection since it defines the minimum temperature at which sufficient fuel vapors are evolved to form an ignitable mixture through which flame can propagate down to the surface of the liquid. Various flash point testers, closed and open cup types, have been developed for making this measurement. A Tag open cup tester (ASTM D1310)^{1/} is currently specified for classifying flammable liquids in government regulations^{2/} concerned with the transportation of hazardous materials. However, the open cup method frequently yields values which tend to underestimate the flammability hazard that may be encountered. At the request of the Department of Transportation, the Bureau of Mines has examined the limitations of various flash point testers for classifying the flammability hazard of combustible liquids and has summarized its findings and recommendations in this report.

Flash Points and Lower Flammable Limits

With any liquid that is combustible in air there is a threshold temperature (flash point, T_f) at which vapors from the liquid can form a vapor-air mixture of concentration equal to the lower limit of flammability, L_t . This is illustrated with data for n-heptane as shown in figure 1. The flash point shown, 22.9° F, is the grand average of 80 measurements contributed during an ASTM-sponsored study.^{3/} The vapor pressure of n-heptane at this temperature is 8.40 torr, corresponding

-
- ^{1/} American Society for Testing and Materials, Flash Point of Volatile Flammable Materials by Tag Open Cup Apparatus; ASTM D1310, 1967.
^{2/} Agent TC George's Tariff No. 23, Hazardous Materials Regulations of the Department of Transportation, Subpart C-Flammable Liquids, 173.115, 1969, p. 61.
^{3/} Work cited in footnote 1.

to 1.10 percent n-heptane in air at one atmosphere. The lower flammable limit of n-heptane in air is 1.05 percent^{4/} at 25° C (77° F) and the temperature coefficient of the lower limit is given by

$$\frac{L_T}{L_{77}} = 1 - 0.00040 (T - 77), \text{ T in degrees Fahrenheit.}$$

The intersection of the lower limit line (dashed) and the vapor pressure curve indicates that n-heptane yields flammable vapor-air mixtures at liquid temperatures above 22.2° F.

While the close agreement between 22.2 and 22.9° F may be fortuitous, figure 1 does illustrate that flammable limit values provide a semi-independent check on the reasonableness of measured flash points. In practice, both measurements are likely to err on the high side, that is, toward an optimistic estimate of hazard. Table 1 shows that flash points provide a less conservative figure generally than do flammable limits although the differences are not large when flash points are close to room temperature.

Table 1. - Comparison of Flash Points Obtained by Tag Closed Cup^{a/} and by Inference From Lower Flammable Limits.^{b/}

Fuel	Observed Flash Point, °C	Calculated Flash Point, °C
Methyl ethyl ketone	-5	-11
Ethyl acetate	-2.2	-5.5
Toluene	7.8	5.0
Methanol	11.1	9.8
Isopropanol	13.9	12.5
Xylene	27.2	27
2-nitropropane	28.3	27.0

^{a/} Work cited in footnote 5.

^{b/} Work cited in footnote 4.

Some part of the difference between the observed and calculated flash points of table 1 may be ascribed to the fact that flammable limits are usually obtained in upward flame propagation while flash point testers rely on horizontal or downward propagation. The flammable range is always somewhat wider in upward propagation because of buoyancy; this is a small but nonetheless real consideration which amounts to about 1.3° F in the flash point of methanol.

^{4/} Zabetakis, M. G., Flammability Characteristics of Combustible Gases and Vapors, BuMines, Bulletin 627, 1965, 121 pp.

Comparison of Flash Point Test Methods

Several test methods are recommended by the American Society for Testing and Materials for determining the flash points of petroleum products and other flammable liquids. Four of the most common types used in this country are listed in table 2. Of the four testers listed, the Cleveland open cup is the least reliable one. The poor reproducibility of data by this tester is attributed partly to the prescribed high heating rate and the poor temperature control that results from the use of an open flame for heating the cup; the presence of air convection currents can also affect the results noticeably. Although the Tag open cup uses a temperature bath and a low heating rate, its precision is still not quite as high as that of the Tag closed cup. Regardless of the precision of the testers, it is equally important to examine the great differences that are frequently obtained for the flash point of a material by the use of the open and closed cup methods.

Table 2. - ASTM Specifications and Measured Performance for Several Flash Point Testers.

Tester	ASTM Designation	Temperature Range, °F	Heating Rate, °F/min	Repeatability, °F	Reproducibility, °F
Cleveland Open Cup	D 92-66	>175	9-11	15	30
Tag Open Cup	D 1310-67	0-200	2	4	7
		201-325	2	9	12
Tag Closed Cup	D 56-64	<55	2	2	6
		55-175	2	2	4
Pensky-Martens Closed Cup	D 93-66	<220	9-11	4	6
		>220	9-11	10	15

Generally, the flash points of flammable liquids are lower by the closed cup than by the open cup method. The amount of the difference will vary with the compositions of the liquids and the models of testers used. The results of a recent study by the Chicago Society for Paint Technology^{5/} with 27 solvents showed the following statistical correlations (°F) between four of the six flash point testers that were used; the

^{5/} Probst, K. G., Correlation of Apparatus for Measuring Flash Point Solvents, Jour. of Paint Technology, Vol. 40, No. 527, December 1968, p. 576.

solvents were hydrocarbon types with flash points between 15° and 200° F:

$$\text{Cleveland O.C. Value} = 1.061 \times \text{Tag C.C. Value} + 10.3 \quad (1)$$

$$\text{Tag O.C. Value} = 1.074 \times \text{Tag C.C. Value} \quad (2)$$

$$\text{Tag C.C. Value} = \text{Pensky-Martens C.C. Value} \quad (3)$$

The differences between the open and closed cup values in the above study are small compared to those which have been observed for certain other solvents or classes of flammable liquids. Differences up to 50° F or more have been reported in a compilation of flash point data for various combustible liquids.^{6/} It is not unusual for such differences to exceed the reproducibility specified for the open cup testers, particularly the Tag open cup.

The significance of open cup flash points is illustrated by the results of a study^{7/} in which the height of the ignition source was varied. With a Cleveland open cup, it was shown that the flash point of hexanol can vary from 200° F to approximately 150° F when the height of the ignition source above the liquid is decreased from 1.25 inches to 0.125 inches. The flash point of this liquid by the standard procedure was 183° F with the Cleveland open cup as compared to the accepted closed cup value of 145° F. Thus, it is evident that open cup flash points will agree approximately with closed cup values if the ignition source is close enough to the liquid. Conversely, one cannot assume that the open cup flash points obtained by standard methods will indicate the extent of the flammability hazard associated with liquid pools.

According to the available data in the literature the Tag closed cup is suitable for determining flash points of liquids over a temperature range from about 220° F down to at least 0° F. Although it is currently recommended for determinations up to only 174° F, ASTM Committees (D-2 and E-27) are presently proposing that the maximum temperature be increased to 200° or 220° F for use with liquids having a viscosity of 4 centipoise (100° F) or less. For liquids of higher viscosity or higher flash points, the Pensky-Martens closed cup is recommended. However, one can also extend the use of the Tag tester to the higher viscosity liquids by employing a lower heating rate than presently specified. A heating rate of less than 0.5° F/min or a maximum temperature difference of 5° F between the bath and sample have been found suitable for extending the applicability of this tester to thickened fuels and other highly viscous materials.^{8/}

Formation of Flammable Mixtures in Transportation

The formation of a flammable mixture depends on the relative availability of fuel vapor and air (for liquid hydrocarbons at normal

^{6/} Humphrey, H. B. and Morgis, G., Safety With Solvents, BuMines IC 7757, 1957, 25 pp.

^{7/} Burgoyne, J. H., A. F. Roberts, and G. L. Alexander. The Significance of Open Flash Points, J. Inst. Petrol., Vol. 53, No. 527, October 1967, p. 338.

^{8/} Kuchta, J. M., A. L. Furno, G. H. Martindill, and A. C. Imhof, Crash Fire Hazard Rating System for Controlled Flammability Fuels, Federal Aviation Administration Report NA-69-17 (DS-68-25), March 1969, 19 pp.

temperature and pressure, a lower limit mixture comprises about 350 ft³ of air per pound of vaporized fuel). Thus the quickest and easiest formation of flammable mixtures occurs within small confined spaces such as the ullage of a shipping container where the partial pressure of fuel vapor rapidly approaches its equilibrium value. The inflammation of confined homogeneous mixtures can easily lead to damaging overpressures. Fortunately, the presence of an ignition source within such small confinements is a remote possibility. For this small hazard, a closed cup tester is obviously preferable to an open cup.

In the more likely problem of a leaking or ruptured shipping container, the formation of a flammable zone depends on local convection as well as the vapor pressure of the liquid. Under no confinement, as in open air, the zone of flammable mixtures usually comprises a surprisingly thin layer above the surface of the liquid. Air currents typically disperse the vapor and diminish the extent of flammable zone (one special problem is the flammable "vapor trail" which may extend downwind from a massive spill of a volatile liquid, particularly when the fuel has a higher molecular weight than the average for air and wind velocities are low; however, vapor trails are associated with fuels having flash points well below ambient temperature, so that the choice of flash point tester is probably insignificant).

It is worth remembering that the ignition of unconfined pools or streams of fuel represents a hazard of fire rather than of explosion. The rate of burning of liquids is governed not only by the factors that control the rate of vaporization, but also by the heat of combustion. For large diameter pools of many liquids, the burning rate (v_{∞}) tends to be time-independent and is given approximately by the following relationship:^{9/}

$$v_{\infty} = k \frac{\text{Net heat of combustion, } \Delta H_c}{\text{Sensible heat of vaporization, } \Delta H_v} \quad (4)$$

where k is a constant and equal to 0.003 when v_{∞} is in in/min. It is important to note that the burning rate is not directly related to flash point; for example, since the $\Delta H_c/\Delta H_v$ ratio is nearly constant (about 100) for many paraffin hydrocarbons, their burning rates vary only slightly in large pools.

It is often proposed that an open cup more nearly approximates the geometry of a spill situation than does a closed cup. In our judgment, this is a trivial consideration in choosing among the variations of existing apparatus. The actual likelihood of ignition of a spill depends heavily on factors which are beyond the scale of laboratory apparatus, such as the cooling of the liquid surface by evaporation or the gustiness of the atmosphere. The closed cup is preferable because it ordinarily gives a more conservative result.

^{9/} Van Dolah, R. W., M. G. Zabetakis, D. S. Burgess, and G. S. Scott.
Review of Fire and Explosion Hazards of Flight Vehicle Combustibles,
BuMines IC 8137, 1963, 80 pp.

The greatest explosion hazard results from leakage or spillage into surroundings that provide some confinement, such as a railroad box car, a van-type truck, or the hold of a ship. In this situation, convection currents aid the formation of homogeneous vapor-air mixtures and the magnitude of overpressures in confined combustion is usually greatest with homogeneous mixtures. Here again, the closed cup gives the best definition of hazard.

The Special Problem of Fuel Mixtures

In the frequently-encountered case of fuel blends where the various components are of the same family of compounds, the most volatile constituents have the lowest flash point. Therefore the flash point of the mixture increases as the more volatile components evaporate. To obtain a conservative estimate of hazard one needs to minimize handling of the sample and minimize its preheating period in the flash point tester. In particular, a closed cup tester must give much more conservative results than an open cup. Some representative data appear in figure 2; at low concentration of the more volatile JP-4 in the fuel blend, the open cup and closed cup give widely different flash points although the results are more nearly comparable at high concentrations of JP-4. Where the fuel blends are in a confined space, the formation of flammable mixtures will be both temperature and time dependent; thus, in the special case of fuel blends with small concentrations of a low flash point liquid, it is necessary to allow the system to equilibrate in order to obtain an evaluation of the maximum flammability hazard. Again, one may argue that when a fuel blend is spilled in open air the volatiles quickly disappear and the hazard is indeed as estimated by open cup results. However, a regulatory agency has no control over the circumstances of an accidental spill; if the mixture is spilled in a confined space, the more conservative closed cup results are clearly more appropriate.

When the most volatile component of a mixture is inert or flame-inhibiting, the opposite situation prevails. One valid example is a fuel which is handled under a nitrogen blanket as in the transportation of Aerozine-50 (51 wt % hydrazine, 47 wt % unsymmetrical dimethylhydrazine). We have found that the initial vapors from spilled A-50 contain large percentages of nitrogen and poorly-ignitable amines until about 1/2 percent by weight of the mixture has evaporated.^{10/} In this case the flash point must surely decrease with handling in the air and the open cup would probably give more conservative flash points than a closed cup.

^{10/} Burgess, D. S., G. H. Martindill, J. N. Murphy, F. J. Perzak, J. M. Singer, and R. W. Van Dolah. Inerting and Extinguishment of Aerozine-50 with Water and/or CF₃Br, J. Spacecraft and Rockets, Vol. 6, No. 11, November 1969, p. 1259. (BuMines Final Report No. 4053, NASA Purchase Request CC 59100, October 31, 1968).

An even more drastic irregularity is provided by mixtures of a flammable liquid with a volatile extinguishing agent. Figure 3 shows flash points determined here with mixtures of isopropyl alcohol and Halon 233. In these experiments, a mixture of 25 volume percent of the Halon had a 110° F flash point by the open cup and none (or at least a much higher value) by the closed cup. Finally, when the same liquid mixture was placed in a well-stirred closed vessel, the vapors were found to support flame propagation at 73° F. Thus, the ignition hazard of an IPA/Halon 233 mixture is a function of its evaporative history and no single apparatus could be expected to give appropriate results. A study by the British Joint Fire Research Organization^{11/} has also shown how misleading results can be if the evaporative history is neglected in assessing the hazard of solvent mixtures containing halogenated flame inhibiting agents.

RECOMMENDATIONS

Since open cup flash point methods can underestimate the potential fire or explosion hazard in handling and transporting most flammable liquids, it is recommended that a closed cup method be used for this purpose. The closed cup method is more precise and reliable than the open cup method and provides the more conservative estimate of the hazard that can be encountered by the formation of flammable vapor-air mixtures under confined or unconfined conditions. As evidence of its greater reliability, the closed cup method has been accepted by the National Fire Protection Association as the most authoritative in defining a code for flammable liquids;^{12/} the NFPA "Flammable and Combustible Liquids Code" has been adopted by many state or provincial enforcement agencies in this country and in Canada for establishing fire protection laws or regulations.^{13/} The National Academy of Sciences^{14/}, a United Nations agency (IMCO)^{15/} and an International Oil Tanker Terminal Safety Guide (IOTTSG)^{16/} also rely on the closed cup method as a basis for flammability classifications.

For the proposed Department of Transportation regulation,^{17/} it is recommended that a closed cup method, such as the Tag (ASTM D56-64), be specified for classifying most flammable liquids having a flash point of 200° F or less. The flammable liquids can include organic or inorganic

-
- ^{11/} Coleman, E. H. Nonflammable Liquid Mixtures and Safety Solvents, The Industrial Chemist, May 1960, p. 211.
 - ^{12/} Flammable and Combustible Liquids Code, NFPA No. 30, National Fire Protection Assn., 60 Batterymarch St., Boston, Mass., 1966.
 - ^{13/} Fire Protection Handbook, National Fire Protection Assn., 60 Batterymarch St., Boston, Mass., 13th Edition, Section 3, Chapters 1 and 2, 1969.
 - ^{14/} National Academy of Sciences Evaluation of the Hazard of Bulk Water Transportation of Industrial Chemicals, Report to the U. S. Coast Guard, Publication 1465, 1966.
 - ^{15/} Inter-Governmental Maritime Consultative Organization, International Maritime Dangerous Goods Code, Class 3, Inflammable Liquids, London, 1968, pp. 3000-3.
 - ^{16/} Hughes, J. R., The Need for an International Standard on Flammability, Preprint British Institute of Petroleum Symposium, Sept. 19, 1969, Portland Place, London.
 - ^{17/} Work cited in footnote 2.

combustibles such as chemicals, fuels, solvents, paints, varnishes, lacquers, oils, lubricants, and related products with a viscosity of less than 4 centipoise (100° F). Liquids with a higher viscosity and flash point of 200° F or less may also be included if the prescribed heating rate (2° F/min) is reduced to less than 0.5° F/min or the temperature differential between the sample and bath is maintained at 5° F or less; otherwise, the Pensky-Martens (ASTM D93-66) must be used for liquids of such high viscosity. In the case of fuel blends or other liquid mixtures, special test procedures must be used to obtain a realistic evaluation of the flammability hazard. Thus, for a fuel blend containing small concentrations of a constituent whose flash point is lower than that of the other component, the preheating period must be kept to a minimum to obtain a conservative estimate of the flash point by the closed cup. For mixtures in which the most volatile component is an inert or a flame inhibitor, an apparatus that provides adequate mixing and an optimum ullage is necessary.

It is further recommended that a flammable liquid be defined as one with a flash point below 140° F, as determined in a Tag closed cup, and having a vapor pressure not exceeding 40 psia at 100° F. The 140° F break point is suggested because ambient temperatures of this order can be encountered during shipment, particularly in hot climates; this break point is also consistent with the NFPA and IMCO classification systems and that proposed by IOTTSG. In addition, we recommend that flammable liquids be divided into four hazard classes and that the NFPA classification code^{18/} be adopted with certain modifications. The proposed classification system is given below. As noted, this system includes breakpoints of 140° F, 100° F, and 70° F. The selection of 70° F instead of 73° F, as prescribed in the NFPA code, is made because this break point is used in several foreign countries and is proposed in a universal classification system for shore operations.^{19/}

- Class I - Liquids with flash points below 70° F and a boiling point below 100° F.
- Class II - Liquids with flash points below 70° F and a boiling point above 100° F.
- Class III - Liquids with flash points at or above 70° F and below 100° F.
- Class IV - Liquids with flash points at or above 100° F and below 140° F.

^{18/} Work cited in footnote 12.

^{19/} Work cited in footnote 16.

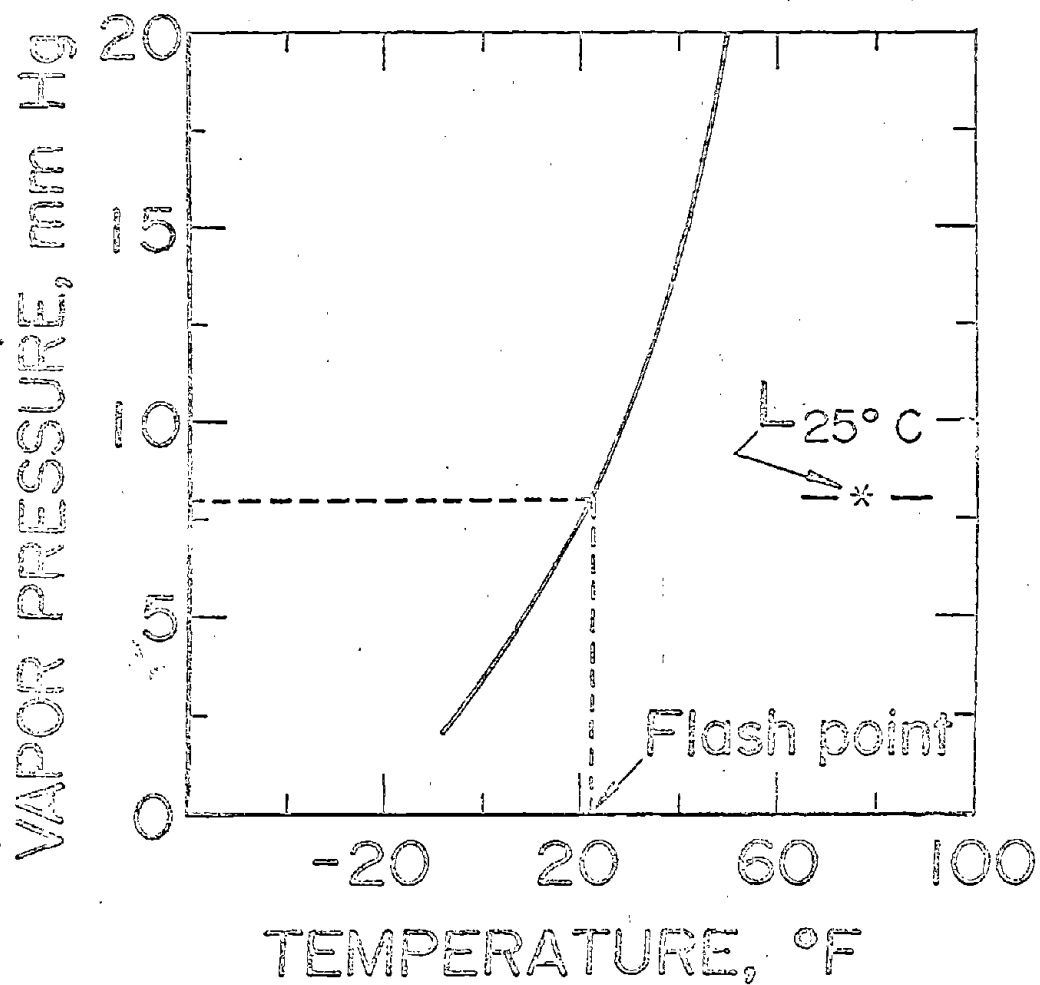


Figure 1. - Vapor Pressure vs Temperature for n-Heptane Showing the Flash Point and Lower Limit of Flammability ($L_{25^{\circ}\text{C}}$) in Air.

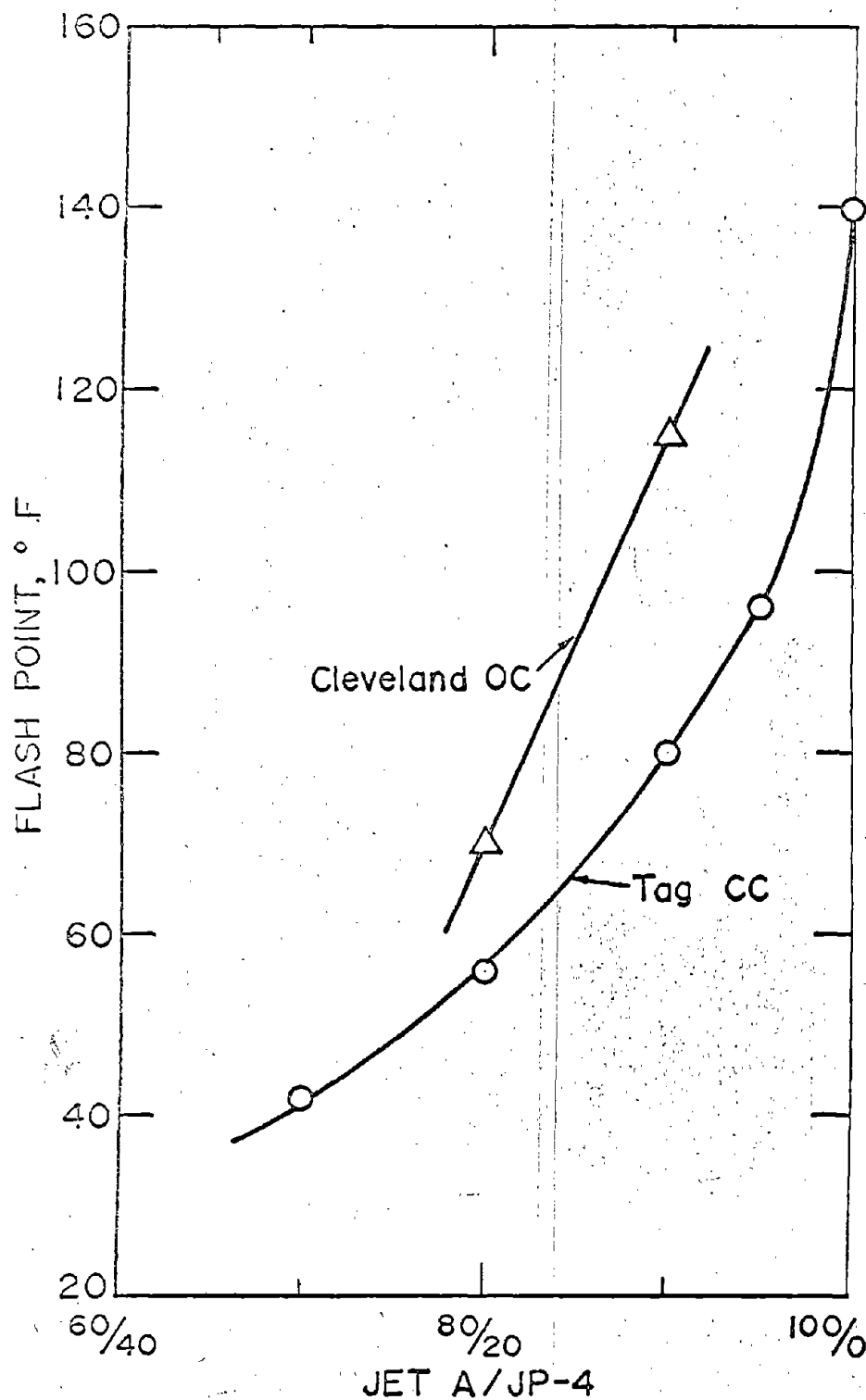


Figure 2. - Flash Points of Jet A and JP-4 Fuel Mixtures by the Cleveland Open Cup and Tag Closed Cup Methods.

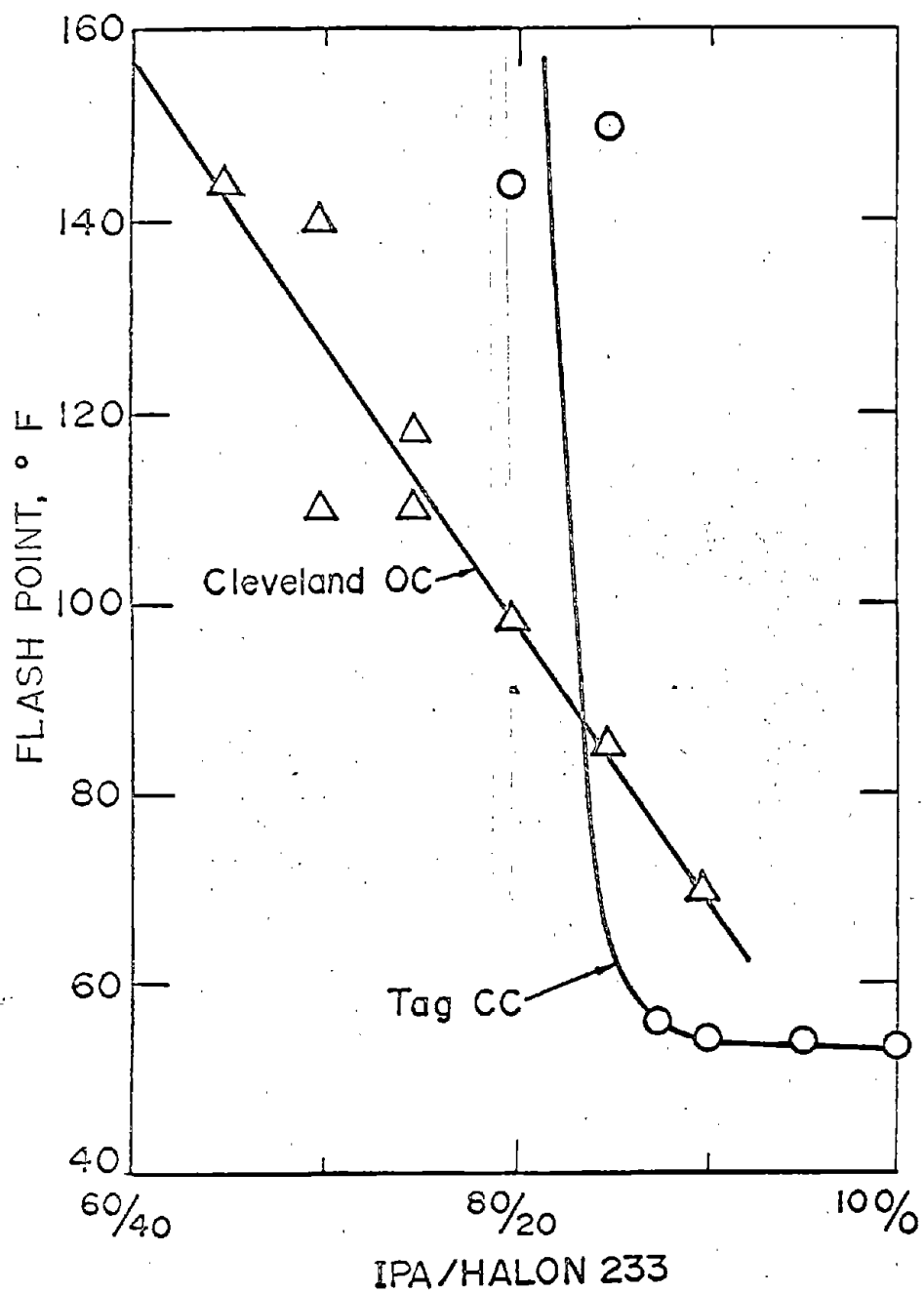


Figure 3. - Flash Points of Isopropyl Alcohol (IPA) and Halon 233 Mixtures by the Cleveland Open Cup and Tag Closed Cup Methods.



United States Department of the Interior

BUREAU OF MINES

4800 Forbes Avenue
Pittsburgh, Pennsylvania 15213

Safety Research Center

ADDITIONAL EVIDENCE IN SUPPORT OF THE CLOSED CUP FLASH POINT METHOD

In the Bureau's recent report^{1/} to the Department of Transportation, the closed cup flash point method was recommended for classifying the flammability hazard of combustible liquids during their transportation. However, various representatives of industry claim the open cup method is more suitable for this purpose and have submitted arguments against a proposed rule change (Docket HM-3),^{2/} which specifies the closed cup for classifying flammable liquids. At the request of the Department of Transportation, further consideration was given to the two methods and additional evidence is given herein in favor of the closed cup method.

One of the arguments considered is that the precision of the improved Tag open cup (ASTM D1310-67)^{3/} is practically the same as that of the Tag closed cup (ASTM D56-64).^{4/} Although the differences in their precision may not be large, ASTM performance evaluations^{3,4/} have established that the reproducibility of the closed cup is significantly better. With the Tag open cup, the average flash points obtained by eight different laboratories varied between 11.8° and 25.2° F for vinyl acetate, 17.2° and 28.5° F for n-heptane, 63° and 73.5° F for isopropanol, and 86° and 95° F for p-xylene. A statistical evaluation of these data indicated that the reproducibility of this tester is 7° F at a 95% confidence level; in comparison, the reproducibility of the Tag closed cup is 4° or 6° F, depending upon the temperature range. Obviously, the precision of the open cup method can be expected to vary with the amount of air convection that may be present. In this connection, it is worth noting the results of an evaluation of flash point testers by committee members of the Chicago Society for Paint Technology;^{5/} they concluded that the closed cup testers are "considerably more reliable" than the Cleveland^{6/} or Tag open cup testers.

-
- 1/ Burgess, D. and J. M. Kuchta, Recommendation of Flash Point Method for Evaluation of Flammability Hazard in the Transportation of Flammable Liquids. BuMines Report No. S4131, April 29, 1970.
 - 2/ Department of Transportation, Docket No. HM-3, Notice No. 68-2, February 27, 1968.
 - 3/ American Society for Testing and Materials, Flash Point of Volatile Flammable Materials by Tag Open Cup Apparatus, ASTM D1310, 1967.
 - 4/ Ibid, Flash Point by Tag Closed Tester, ASTM D46, 1964.
 - 5/ Probst, K. G., Correlation of Apparatus for Measuring Flash Point of Solvents. Jour. Paint Technology, Vol. 40, December 1968, p. 576.
 - 6/ American Society for Testing and Materials, Flash and Fire Points by Cleveland Open Cup, ASTM D92, 1966.

The strongest argument for the Tag closed cup is that the flash points of most flammable liquids are lower by this tester than by any open cup tester. Table 1 compares data that were obtained by different laboratories with the same batch samples of 26 organic solvents.^{5/} As noted, the flash points by the improved Tag open cup (electric) are as much as 20° higher than the corresponding values by the Tag closed cup (electric); also, for most of the solvents, these differences exceeded the ASTM reproducibility specified for the flash point testers. The highest flash point values obtained by the investigators were by use of the Cleveland open cup, although these data are not listed in table 1. Thus, regardless of the specified precision of these testers, the closed cup will generally provide the more conservative estimate of the flammability hazard.

In the case of liquid mixtures, it must be recognized that both the open and closed cup methods can give misleading results. As illustrated in the earlier report,^{1/} one must consider such factors as the amount of ullage, extent of mixing, and the evaporation history to obtain an evaluation of the maximum flammability hazard. The British Joint Fire Research Organization^{7/} also has shown how standard flash point methods can be unreliable, particularly for mixtures where the most volatile component is flame inhibiting. For example, the flash point of a commercial cleaning or degreasing mixture consisting of white petroleum spirit and carbon tetrachloride was found to be 210° F initially, but as low as 101° F when 50 percent of the mixture was allowed to evaporate. Similarly, it was shown that the flammability hazard can be underestimated for a commercial paint stripper of methylene chloride/acetone (10/1) and a grain fumigant of ethylene dichloride/carbon tetrachloride (3/1) unless the evaporative history is considered. To evaluate the flammability hazard of such mixtures, the Underwriters' Laboratories recommends the use of a special closed vessel apparatus equipped with a stirrer to insure adequate mixing of the vapors.^{8/} By this method, the temperature limits of flammability can be noticeably lower than the flash points obtained by the Tag open cup or closed cup methods; this was illustrated in the earlier report^{1/} for isopropyl alcohol-Halon 233 mixtures. Other investigators^{9/} have also cited the misleading flash point results that are possible with such mixtures.

Where the fuel component of a mixture is the more volatile, the problem of defining the flash point is less complicated than with the above mixtures. Table 2 lists closed cup and open cup flash points that have been reported for various ethanol-water mixtures;^{10/} the models of the testers are not known. It is evident that the closed cup method provides the more conservative estimate of the flammability hazard for these mixtures.

7/ Coleman, E. H., Nonflammable Liquid Mixtures and Safety Solvents. The Industrial Chemist, May 1960, p. 211.

8/ Underwriters' Laboratories Inc., Test Methods for Carbon Disulfide-Carbon Tetrachloride Base Fumigants, Subject 340, July 20, 1955.

9/ Coffee, R. D., Pitfalls and Interpretations-Some Aspects of Hazard Evaluation Testing. Presented at 1967 National Safety Congress, Chicago, Ill., October 26, 1967.

10/ Mellan, I., Industrial Solvents, 2d Edition, Reinhold Publishing Co., New York, 1950, p. 207.

TABLE 1. - Comparison of Flash Points of Various Solvents by the Tag Open Cup and Tag Closed Cup.^{a/}

Solvent	Flash Points, °F		
	Tag Open Cup ASTM D1310-67	Tag Closed Cup ASTM D56-64	Difference
Toluoil	24	21	3
Methyl ethyl ketone	28	21	7
Ethyl acetate	34	21	13
Toluene	48	44	4
Methanol	55	49	6
Apcothinner	63	51	12
Isopropanol (99%)	62	56	6
Methyl isobutyl ketone	67	60	7
Xylene	89	79	10
2-Nitropropane	85	84	1
N-Butyl acetate	88	79	9
N-Butanol	106	99	7
Mineral spirits #10	116	103	13
Polysolv EM	109	103	6
250 W-Hi-flash naphtha	120	107	13
Methyl isobutyl carbinol	114	108	6
Comsolv #4	124	112	12
Comsolv #100	121	111	10
Kerosene #50	146	126	20
Dimethyl formamide	145	137	8
Solvent #140	152	140	12
Comsolv #150	156	146	10
Polysolv EB	155	143	12
Comsolv #6	168	154	14
Dimethyl sulfoxide	196	190	6
M-Pyrol	204	190	14

^{a/} Data from reference in footnote 5.

14

TABLE 2. - Flash Points of Ethanol-Water Mixtures.

<u>Ethanol, Vol. %</u>	<u>Flash Point, °F</u>	
	<u>Closed Cup</u>	<u>Open Cup</u>
100	56	65
95	61	75
85	67	80
70	71	90
55	77	95
40	83	105
25	94	115

It is also argued by some proponents of the open cup method that the flash points by the Tag closed cup and Tag open cup do not necessarily differ by a constant value such as the 10° F difference suggested in the proposed rule making.^{2/} The Bureau agrees with this argument (see Table 1) but considers it to be further evidence of the poor reliability of the open cup.

We conclude that the best choice for classifying flammable liquids is the Tag closed cup tester whose scope is currently being increased by two ASTM committees (E-27 and D-2) to permit its use at higher temperatures, at least to 200° F, and with a greater variety of flammable liquids.

