SOLVENTS

Flash Points of Oxygenated Solvents

in Aqueous Systems

EASTMAN

Contents

In the formulation of coatings, it is necessary to have a thorough knowledge of flash point behavior under a variety of conditions. Since coatings are routinely stored in sealed containers that provide vapor-phase headspace above the liquid and since potential often exists for exposure to a flame, flash point value is a major concern of manufacturers, applicators, and insurance companies alike (Figure 1).

In both coatings and inks, some “binder” system is usually present. In dilute solutions, this binder may be assumed to have little influence on the flash point value. However, in extremely high-viscosity resinous mixtures, the equilibrium of the solvent between the solid and vapor phases may be significantly altered, shifting the flash point value. Under such conditions, elevation in the flash point value of the system is expected. This publication discusses only the volatile part of the coating or ink and its influence on flash point.

Flash point is defined as “the lowest temperature at which vapors above a volatile combustible substance ignite in air when exposed to flame.” Flash point value will depend on the flash point of the individual components of a mixture as well as on the conditions under which the flash point is determined.

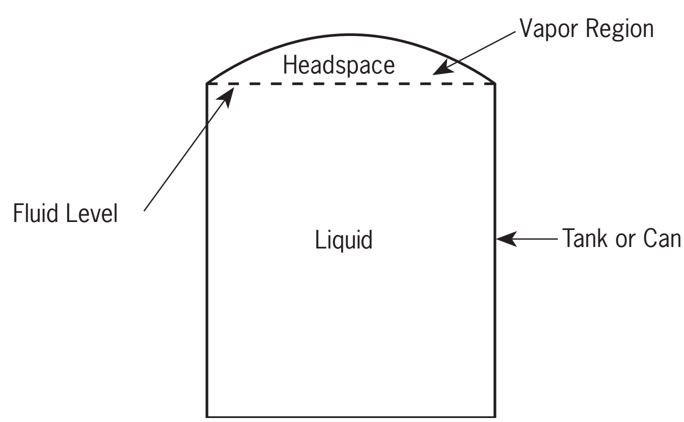
Some methods for determining flash points are Tag closed cup, *Cleveland* open cup, *Pensky-Martens* closed cup, Tag open cup, and Setaflash. Each of these methods is designed for a particular sample profile, and the choice of method should be based on viscosity level, temperature range, nonvolatile content, and physical behavior of the system under a given set of test conditions. The Utopia Instrument Company has assembled a chart that summarizes some of these flash point methods. [1]

Most concerns over flash point values arise because the flash point of the composition is too low, not too high. Thus, the challenge in the majority of situations is to elevate the flash point value of the volatile composition to an acceptable level by an appropriate technique.

OSHA classifies materials with flash point values below 100°F as “flammable” and those with flash point values greater than 100°F as “combustible” as shown in Figure 2.

Under DOT regulations, flammable materials have flash points below 141°F while combustible materials have flash points between 142° and 200°F. However, the DOT does allow an exemption to these fire

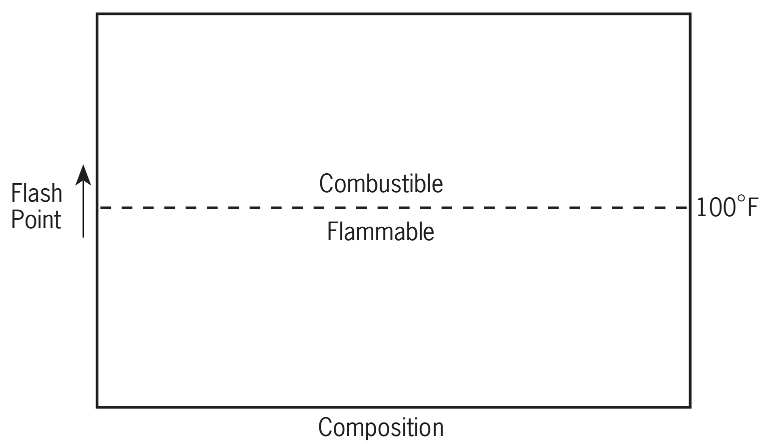
Figure 1
Sealed Containers Provide Vapor-Phase Headspace Above the Liquid



hazard classifications when materials are shipped by land in less than bulk quantities. In this case, materials with flash points less than 100°F are classified as flammable and those with flash points greater than 100°F are classified as combustible.

From a safety vantage point, the label “combustible” is more desirable than “flammable.” One obvious goal of flash point experiments is to develop methods of elevating the flash point value while maintaining attractive economics and balancing properties such as solvency power, evaporation rate, rheological characteristics, and odor, along with an acceptable toxicological profile.

Figure 2
At 100°F, the OSHA Fire Hazard Classification Changes From Flammable to Combustible



Experimental

The purpose here is to examine the flash points of oxygenated solvent/water compositions. The oxygenated solvents of interest include heterocyclic ethers, glycol monoethers, alkyl alcohols, glycol monoether esters, ketones, and esters. Only solvents which possess an appreciable degree of mutual aqueous miscibility are considered. [2]

A Setaflash instrument was used to measure flash point. Setaflash values agree quite well with Tag closed cup values.

Both binary and ternary systems were examined. The binary systems consisted of oxygenated-solvent/water compositions in which the oxygenated solvent structure in the composition was varied. Systems with water concentrations greater than 80% were of primary interest since formulated waterborne systems frequently contain water levels in the 80% concentration range. The ternary systems studied consisted of glycol monoether/alkyl alcohol/water. As shown in Table 1 and Figure 3, the aqueous fraction was held constant while the relative amounts of glycol monoether to alcohol in the organic fraction were varied over the range of 100/0 to 0/100 in 10 wt % increments. Ethylene glycol monobutyl ether (*Eastman* EB solvent) represented the glycol monoether component.

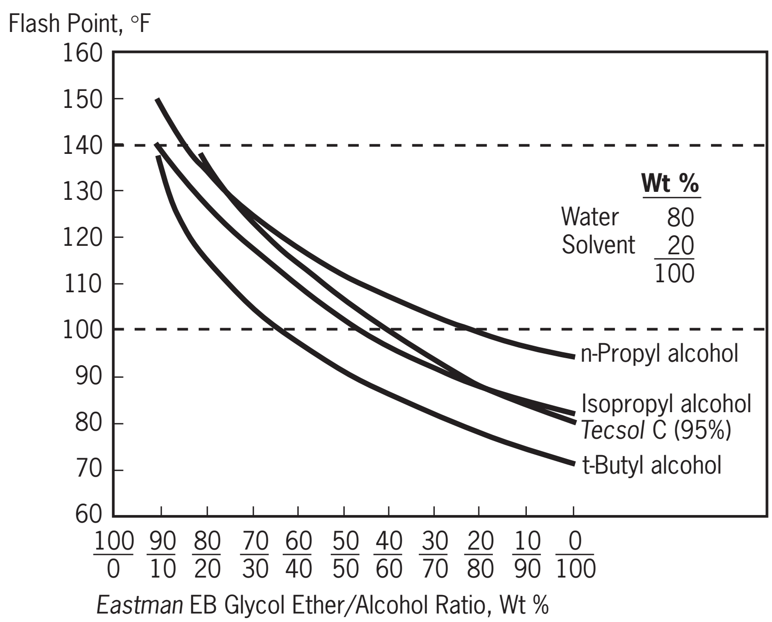
Table 1

Ternary System Evaluated

	Wt %
Fixed-Water	80
Variable (*Eastman* EB Solvent) Ratio (Alkyl Alcohol)	20
	100

Flash point was studied as a function of composition variation over the temperature range of ambient to 200°F. (Above 200°F, complications can arise due to the increased rate of volatilization of water.)

Figure 3
Flash Points of Oxygenated Solvents in Aqueous Systems



Results

Frequently, formulators of coatings and inks seek a combination of fast evaporation rates and flash point values above the 100°F reclassification line. Table 2 shows that this combination of properties [3] is extremely difficult to achieve when formulating with mixtures or pure organic solvents. Evaporation rate and flash point values of oxygenated solvents demonstrate an inverse relationship with respect to one another. The flash point of oxygenated solvents normally increases as the molecular weight and boiling range are increased; evaporation rate, as a rule, diminishes under these conditions.

Table 2

Comparative Flash Point Properties

Solvent	Evaporation Rate	Flash Point, °F TCC[a]	Flash Point, °F TOC[b]	Boiling Range °C 760 Torr	Molecular Wt, Grams
Ketones and Heterocyclic Ethers					
Tetrahydrofuran	6.3	—	4	65–67	72.10
Acetone	7.7	–4	–2	55–57	58.08
MEK	3.8	16	26	78–81	72.10
Diacetone Alcohol	0.1	—	136	169–172	116.16
Glycol Ethers					
Ethylene Glycol Monomethyl Ether	0.5	102	111	123–125	76.10
Ethylene Glycol Monoethyl Ether	0.3	110	118	134–136	90.12
Eastman EB Solvent	0.1	143	158	169–173	118.17
Eastman DM Solvent	0.02	191	205 COC[c]	191–198	120.15
Eastman DE Solvent	0.02	195	205 COC	198–204	134.17
Eastman DB Solvent	>0.01	—	232 COC	227–235	163.23
Esters and Glycol Ether Esters					
Ethylene Glycol Monomethyl Ether Acetate	0.4	120	125	140–147	118.13
Ethylene Glycol Monoethyl Ether Acetate	0.2	130	139	150–160	132.16
Ethyl Lactate	0.2	—	130	119–172	118.13
Ethylene Glycol Diacetate	0.02	191	210 COC	187–193	146.15
Eastman DE Acetate	<0.01	—	225 COC	214–221	176.21
Alcohols					
Methyl Alcohol	3.5	52	62	64–65	32.07
Tecsol C (95%) Ethanol	1.7	56	—	78[d]	46.07
Isopropyl Alcohol	1.7	55	60	82–83	60.09
n-Propyl Alcohol	1.0	74	81	96–98	60.09
sec-Butyl Alcohol	0.9	—	80	98–101	74.12
tert-Butyl Alcohol	1.0	52	—	83[d]	74.12

[a] *Tag closed cup.*
[b] *Tag open cup.*
[c] Cleveland *open cup.*
[d] *Boiling point.*

Some anomalies do exist. For example, methyl ethyl ketone and tetrahydrofuran have identical molecular weights (isomeric), yet the boiling range and flash point for the ketone are substantially higher than for the heterocyclic compound. The molecular weight is identical, but the evaporation rate of tetrahydrofuran is 65.8% faster than that of methyl ethyl ketone.

Other anomalies are evident among the isomeric propyl and butyl alcohols. Although the propyl isomers have identical molecular weights, the flash point value and boiling range of the normal isomer are greater than that of the branched isomer. Isopropyl alcohol evaporates 70% faster than n-propyl alcohol. A similar comparison can be made on the isomeric butyl alcohols. The more extensively branched tertiary butyl alcohol evaporates only 11% faster but has a flash point value and boiling range that are notably lower than those of the secondary butyl alcohol structure.

When an oxygenated solvent is placed in an aqueous medium to form a binary system, the flash point trend will depend on the interaction within the composite and the relative component concentrations. A series of organic solvents were compared at 80/20, 90/10, and 95/5 water-to-solvent weight ratios, as seen in Table 3. Setaflash values were obtained according to ASTM D 3278.

Table 3

Binary Systems—Aqueous/Organic Solvent Setaflash Flash Points (°F), ASTM D 3278

	H_2O/Solvent Weight Ratios		
Organic Solvent	**80/20**	**90/10**	**95/5**
Ketones and Heterocyclic Ethers			
Tetrahydrofuran	41.0	42.5	61.0
Acetone	36.7	56.7	78.2
MEK	32.5	48.5	66.5
Diacetone Alcohol	*	*	*
Glycol Ethers			
Ethylene Glycol Monomethyl Ether	*	*	*
Ethylene Glycol Monoethyl Ether	*	*	*
Eastman EB Solvent	*	*	*
Eastman DM Solvent	*	*	*
Eastman DE Solvent	*	*	*
Eastman DB Solvent	*	*	*
Esters and Glycol Ether Esters			
Ethylene Glycol Monomethyl Ether Acetate	147.2	*	*
Ethylene Glycol Monoethyl Ether Acetate	138.3	146.3	*
Ethyl Lactate	*	*	*
Ethylene Glycol Diacetate	**	*	*
Eastman DE Acetate	*	*	*
Alcohols			
Methyl Alcohol	97.1	137.6	*
Tecsol C (95%) Ethanol	77.5	105.0	130.5
Isopropyl Alcohol	82.5	98.0	118.5
n-Propyl Alcohol	95.2	106.7	125.2
sec-Butyl Alcohol	84.0	90.5	106.5
t-Butyl Alcohol	72.0	86.5	103.0

**No flash point noted over test range evaluated.*
***Immiscible at room temperature.*

Of the ketones and heterocyclic solvents examined, three systems displayed flash points at each water concentration tested. The Setaflash values were below 100°F even in the presence of 95% water. Extremely volatile oxygenated solvents possessing low flash points in the pure state are difficult to quench, even with large amounts of water. The 95/5 water-to-solvent system remained below 100°F in Setaflash value. Tetrahydrofuran, which had a flash point in the pure state far below that of the methyl ethyl ketone isomer when blended in the aqueous systems, had a flash point closely approximating the corresponding methyl ethyl ketone/water systems. As shown in Figure 4, the composition dependence of the flash point varies for methyl ethyl ketone versus tetrahydrofuran.

The addition of water was quite effective in raising the flash point of the majority of glycol monoether, esters, and glycol monoether esters tested. Ethylene glycol monoethyl ether acetate and ethylene glycol monomethyl ether acetate did exhibit flash points in the combustible classification region. Although ethylene glycol monomethyl ether acetate was lower in molecular weight, boiling range, and flash point in the pure state, it was more rapidly elevated in Setaflash value in the binary system by the sequential addition of water.

A solvent can possess a combination of higher evaporation rate in the pure state and higher flash point value in a binary aqueous system. However, the evaporation rate of an oxygenated solvent in the pure state is not necessarily the same as in an aqueous mixture. Hydrogen bonding forces may result in deviation from ideal evaporation curves.

The alcohol/water systems may be the most interesting binaries to examine, since it is often desirable to elevate their flash points above 100°F. At the 80/20 ratio (water/solvent), each system had values below 100°F and, thus, were classified as flammable (refer to Table 3). The lowest flash point was obtained when using tertiary butyl alcohol. Tertiary butyl alcohol and methyl alcohol have the same Tag closed cup flash point value in the pure state. However, when placed in a binary aqueous environment at identical wt % concentrations, the Setaflash value for the methyl alcohol systems was 25.1°F higher. The tertiary butanol system possessed the lowest flash point value through the entire aqueous range surveyed. As seen in Figure 4, methyl alcohol and *Tecsol* C (95%) solvent responded quickly to flash point elevation by addition of water. The higher alkyl homologs responded to elevation, but at a less rapid pace. At the 95/5 ratio, each mixture acquired a flash point greater than 100°F.

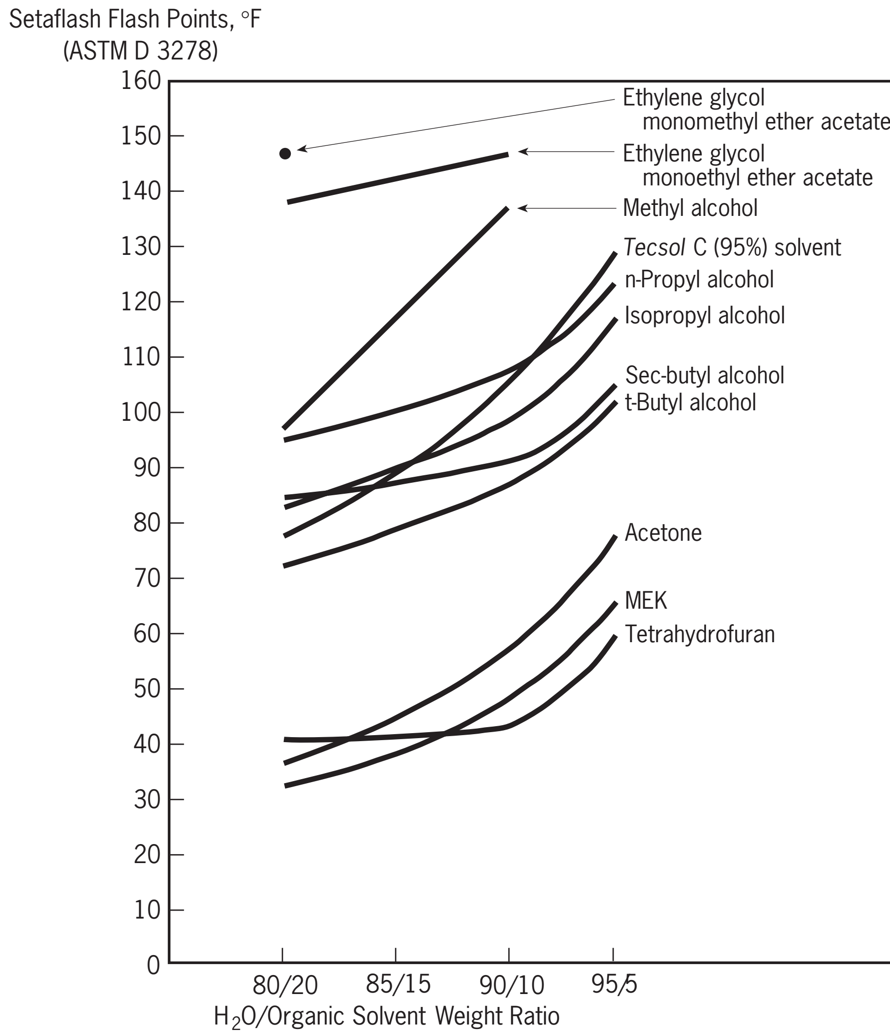
Although an ink formulation may rely on binary systems, such as alcohol/water or glycol monoether/water combinations, to perform the function of the volatile fraction, more sophisticated ternary systems are popular in waterborne paints. Starting mixtures typically contain 80% water and 20% organic component, normally alcohols and glycol ethers. The ratio of alcohol and glycol monoether can be varied to obtain an acceptable combination of solvency, evaporation rate, and economics.

A series of ternary compositions were evaluated (see Figure 3). Each system contained 80% water and 20% organic solvent. The flash point value of each mixture was monitored as the glycol monoether/alcohol ratio present in the organic fraction was varied. *Eastman* EB solvent was used as the glycol monoether. Four respective alkyl alcohols were tested. The alcohols included tertiary butyl alcohol, *Tecsol* C (95%) solvent, isopropyl alcohol, and n-propyl alcohol.

Tertiary butyl alcohol caused the most rapid decline in Setaflash value as a function of concentration. The addition of 35% to the organic phase, or approximately 7% to the total system, reduced the flash point value to the 100°F temperature. *Tecsol* C (95%) solvent or isopropyl alcohol could be added as 50% to 60% of the organic fraction before the flash point dropped below 100°F. A maximum of 78% of the organic solvent was n-propyl alcohol before the system moved from the combustible to the flammable region.

Figure 3 clearly demonstrates that increasing the alcohol content, at the expense of the glycol monoether, substantially reduces the Setaflash value of the system. Conversely, the flash point of an aqueous alcohol mixture can be elevated through the addition of glycol monoether at the sacrifice of alcohol content. The ratio of high boilers to low boilers in the organic solvent at constant water content can be used to control the flash point.

Figure 4
Flash Points of Various Water/Organic Solvent Compositions



Conclusions

The data presented in this publication is by no means all-inclusive. The relationship of flash point to evaporation rate, boiling range, and molecular weight has been used to illustrate the practical limitations of adjusting flash point values versus maintaining other system properties. Systems with phase separation should be avoided to maintain constancy of the flash point composition. Additional insight into flash point behavior could result from investigating such fundamental properties as vapor/liquid equilibrium curves.

The investigations of flash point behavior in binary and ternary aqueous solvent systems do suggest guidance in the control of the property. The flash point of the binary system can be elevated by altering the water balance to organic component in favor of the water. In ternary systems, adding glycol monoethers with a corresponding reduction in alcohol content elevates the Setaflash value. Use of alcohols with high flash points in the pure state can produce systems with lower costs and higher flash points.

References

1. Utopia Instrument Co., "Flash Point Test Summary Chart," P.O. Box 863, Joliet, Illinois 60434.

2. Culver, L. J., and Grant, P. M., "Miscibility Characteristics of Organic Solvent/Water Mixtures for Waterborne Coatings," *American Paint and Coatings Journal,* September 24, 1979.

3. Eastman Publication M-167, *Eastman Solvent Selector Chart*.

EASTMAN

Eastman Chemical Company
Corporate Headquarters
P.O. Box 431
Kingsport, TN 37662-5280 U.S.A.

Telephone:
U.S.A. and Canada, 800.EASTMAN (800.327.8626)
Other Locations, (1) 423.229.2000
Fax: (1) 423.229.1193

www.eastman.com

Eastman Chemical Latin America
9155 South Dadeland Blvd.
Suite 1116
Miami, FL 33156 U.S.A.

Telephone: (1) 305.671.2800
Fax: (1) 305.671.2805

Eastman Chemical B.V.
Fascinatio Boulevard 602-614
2909 VA Capelle aan den IJssel
The Netherlands

Telephone: (31) 10 2402 111
Fax: (31) 10 2402 100

Eastman Chemical Japan Ltd.
AIG Aoyama Building 5F
2-11-16 Minami Aoyama
Minato-ku, Tokyo 107-0062 Japan

Telephone: (81) 3.3475.9510
Fax: (81) 3.3475.9515

Eastman Chemical Asia Pacific Pte. Ltd.
#05-04 Winsland House
3 Killiney Road
Singapore 239519

Telephone: (65) 6831.3100
Fax: (65) 6732.4930

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