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Hazard Ratings of Vapors from Coatings and Adhesives

ABSTRACT: Many coatings and adhesives have components that are flammable and/or have toxic hazard. When such materials are associated with personal or property injury leading to litigation, there is often the question as to magnitude of hazard. How does the involved material compare to alternative materials suitable for the same task?

This paper presents methods for comparing such materials, using a number of commercial coatings and adhesives as examples for the comparison. The authors present a concept of Flammable Hazard Index whose numbers may range from zero to 20 billion among the population of commercial materials. Inhalation hazards are also compared using a toxic injury potential (TIP), which is the volume of air required to dilute the vapors to permissible exposure limits (PEL) suitable for 8-hour work-day exposure.

KEYWORDS: forensic science, flammability, toxicity, hazards, ventilation, adhesives, coatings, ratings

Coatings and adhesives find their way into the forensic arena as causes of fires, explosions, and inhalation injury.

This paper provides equations whereby an expert witness (fire investigator or toxicologist) can compare the relative dangers of products in terms of both flammability/explosion hazard and toxicity hazard from breathing the vapors. This paper does not address in detail all of the application or causation factors that might relate to a specific fire or inhalation incident.

Although the calculations and data presented here use coatings and adhesives as examples, the methods are equally appropriate for organic solvents and other mixtures thereof.

Adequacy of Ventilation

Practically all labels of products having flammable or toxic components say, "Use adequate ventilation." The test of ventilation adequacy is then rather empirical—if use was successful without fire, explosion or toxic reaction, the ventilation was adequate. If an accident occurred, the ventilation was not adequate, and the product manufacturer will say that the user was at fault.

OSHA requires that materials with flash point below 100°F be sprayed in a paint spray booth with 100 foot/minute frontal velocity [1]. This is the only definition of "adequate ventilation" that we have seen in an authoritative reference. Hazardous lacquers, contact adhesives and floor-covering adhesives are often used in home or office environments where adequate ventilation can not be attained to ensure safe use of these materials, and the use of minimal hazard materials is imperative if more than minimal quantities are involved.

Background

Flammability of vapors is well discussed in publications of the National Fire Protection Association [2,3] and in OSHA regulations. Flash point temperature is usually the basis for comparing relative hazards of different chemicals, and this basic criterion is defined in the NFPA citations [2,3]. If use temperature is cooler than the flash point temperature, the material has insufficient vapor concentration to ignite and there is less fire hazard. The Hazardous Materials Labeling Act classifies materials as "extremely flammable" if the flash point is less than −7°C (20°)F, "flammable" if flash point is between −7° and +38°C (20° and 100°F), and "combustible" if the flash point is higher [4]. These are not the same as ratings used by NFPA and OSHA [2,3]. The flash point is physically related to the vapor pressure and the lower explosive limit of the vapor, as noted for a number of solvents in Fig. 1. The Consumer Products Safety Commission has used flash point as criterion for banning the sale of "extremely flammable" contact adhesives to the public in packages larger than 236 mL (8 fluid ounces) [5]. If a single criterion of flammability hazard is to be used, flash point is the best, but the hazard also relates to the severity of fire or explosion—the amount of energy evolved upon combustion of the vapors.

For example, a 1 gallon can of gasoline has combustion energy comparable to 14 large sticks of dynamite [6] or to 20.5 kg (45 pounds) of TNT. A gasoline explosion may not have the same percussive pressure as the TNT, but its vapors can explode and it has an equal fire hazard on the basis of total energy.

Although methyl alcohol and octane have approximately the same flash points, 12° and 16°C (54° and 60°F), the energies of combustion of these materials are very different, 18 and 25 million joules/liter (64,500 and 89,500 Btu/gallon) respectively. Thus we consider vapors of octane to be a significantly greater hazard than vapors of methyl alcohol when used at ambient temperature of 24°C (75°F).

The hazard of toxic vapors is generally indexed by the Tolerable Level of Vapors (TLV) or the Permissible Exposure Level (PEL). The TLV is published by the American Council of Governmental and Industrial Hygienists. The PEL is published by OSHA. Both of these identify the maximum safe concentration, and a low TLV or PEL means a high toxicity hazard.

However, the hazard also relates to the rate of evaporation of the toxic chemical, and a slowly evaporating material with high toxicity (for example, butyl cellosolve) could be less hazard than a fast evaporating material with low toxicity (for example, hexane) depending upon the nature of ventilation to remove the vapors as they are formed.

The rate of evaporation is sometimes reported, relative to a reference material such as ethyl ether or n-butyl acetate. A high vapor pressure (frequently reported in the Material Safety Data Sheet, MSDS) will always mean fast evaporation, but the heat of evaporation and the solvent/solute interaction may significantly affect the rate of solvent release. The vapor pressure can be used to calculate the local maximum vapor concentration at the surface of the liquid if it is a pure solvent.

Rate of evaporation tests can be performed on specific materials, applied to an appropriate substrate by brush or spray to proper thickness (labels usually state coverage in terms of square feet/gallon). With the substrate in pertinent orientation (horizontal or vertical) the
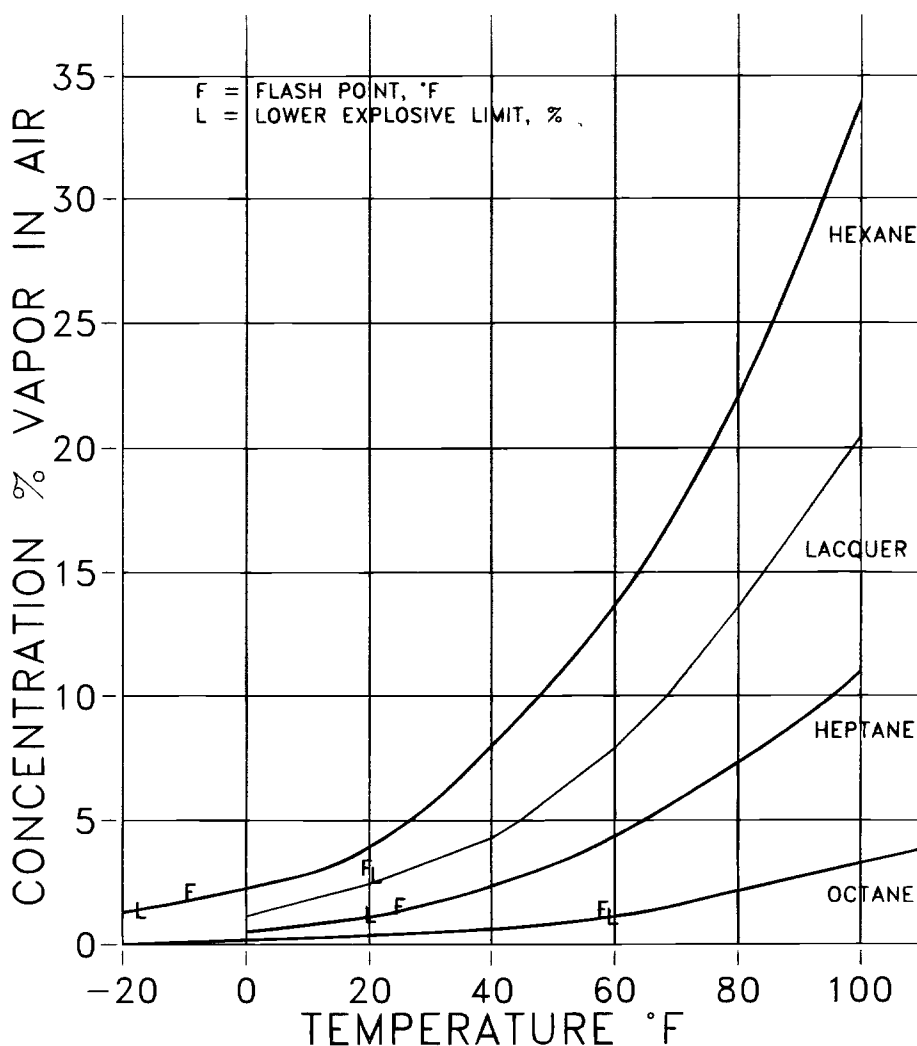
FIG. 1—*Relationship of flash point and LEL to vapor pressure and temperature.*

material is allowed to evaporate. The substrate can be weighed at frequent intervals to learn the rate of weight loss (volatiles). From the weight loss, the rate of generation of explosive or toxic cloud can be calculated using average properties of the solvent vapors. Figures 2 and 3 present experimental data of this nature for a sanding sealer that was involved in litigation due to fire injury and damage.

Because most commercial products involve a blend of solvents with hazardous vapors, a rating system of relative hazards requires a combination of hazards from each individual component. For flammable and toxic materials, the hazards are considered additive [7,8].

Flammability/Explosion Rating

The obvious factors contributing to the flammability and explosion hazard for a particular product are listed in Table 1A. The factors listed in Table 1B are important in relation to a particular accident investigation.
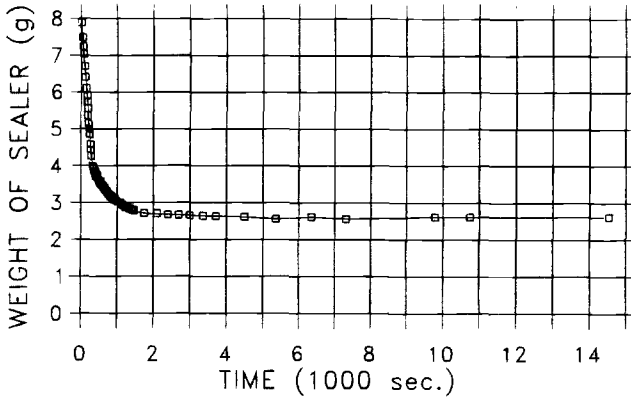
FIG. 2—*Weight of plywood and coating as function of drying time, vertical orientation.*

The flash point of the mixed product is usually stated in the MSDS. We have seen a number of wrong flash point data entries or wrong test methods in MSDS reports so we suggest testing this. We have also tested the flash points of coatings at 1 mile altitude observing flash at temperatures much less than expected from the usual ASTM correction factors for altitude. One coating had actual flash temperature 21°C (38°F) below the sea level flash point (vs about 5°C difference expected for a pure solvent). This means that
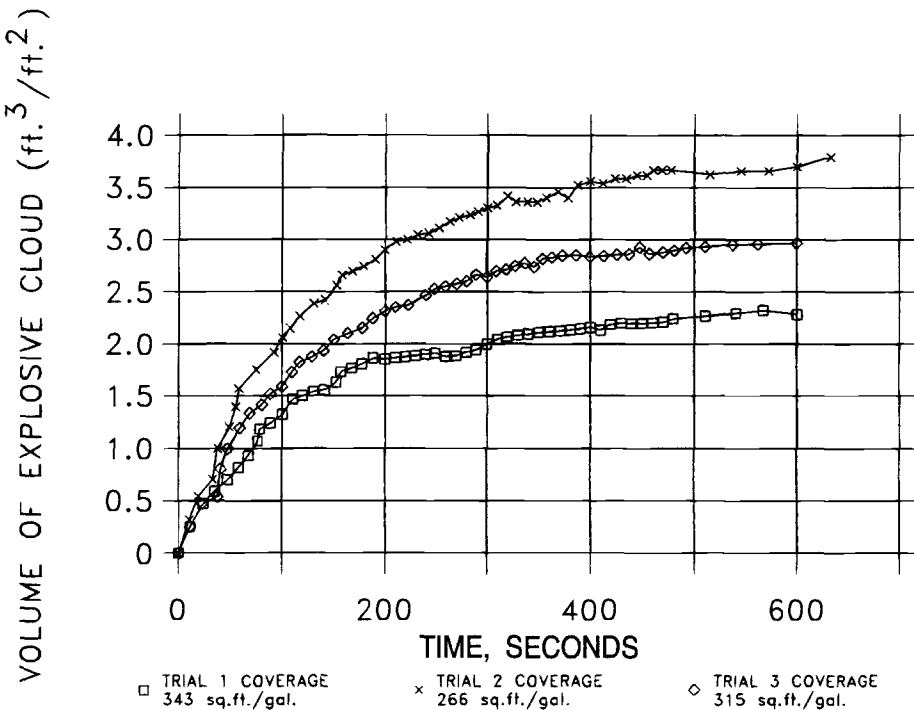
TRIAL 1 COVERAGE
343 sq.ft./gal.

TRIAL 2 COVERAGE
266 sq.ft./gal.

TRIAL 3 COVERAGE
315 sq.ft./gal.

FIG. 3—*Laboratory tests of weight loss vs time permit calculation of accumulated explosive cloud volume; the coverage has a notable effect.*

TABLE 1—*Product hazards.*

	Flammability	Toxicity
A. Product Factors		
Flash point	X	
Lower explosive limit	X	
Volume of explosive cloud	X	
Combustion energy	X	
Heat of vaporization	X	X
Vapor pressure	X	X
Vapor density	X	X
Toxicity of components		X
Volume of toxic cloud		X
B. Usage Factors		
Amount of material used	X	X
Coverage, amount per area	X	X
Volume of enclosure	X	X
Air circulation through work site	X	X
Use temperature	X	X
Altitude (ambient pressure)	X	X
Time	X	X
Application process	X	X

some materials are much more hazardous at high altitudes than as indicated by the MSDS information.

As mentioned, the rate of generation of an explosive cloud can be learned experimentally from the rate of evaporation for a specific application or litigation.

Alternatively, products are often compared without such evaporation tests to inform trier of fact the relative hazards/merits of alternative materials on the market. The total volume of explosive cloud (V_e) can be calculated for a gallon of the original product by combining the vapor volumes for each component based upon the volumes per mole, composition of mixture and LEL of each component:

$$V_e \text{ cu meter/liter} = \Sigma \ (24.2 \ W \ X \ /LEL \ MW) \tag{1}$$
$$V_e \text{ cu ft/gal} = \Sigma \ (390 \ W \ X \ /LEL \ MW)$$

where:

X = weight fraction of component in product
W = density of product, gm/ml or lb/gal
LEL = Lower Explosive Limit in air, in decimal terms
MW = Molecular weight of component in product

This calculation gives the explosive volume at 24°C (75°F) and at sea level pressure from evaporation of 3.78 liters (1 gallon) of product.

The larger the volume of explosive cloud, V_e the more fresh air ventilation is required in order to keep vapor concentration below the lower explosive limit. The V_e or flammable dilution volume for many pure liquids may be found in reference [9], defined there as the volume of air required to dilute 3.78 liters (1 gallon) of liquid to the LEL concentration.

The combustion energy of each component can usually be found in handbooks [10–12] where the energy may be in joules/gram mole, kilocalories/gram, Btu/lb or other units). The Dow Fire & Explosion Index, Hazard Classification Guide [13] lists these with units Btu/lb. Here we convert the energy to energy per volume of mixed product, using the

additional factors of molecular weight, percent composition by weight and density of the product. For chemicals not listed in the usual handbooks, the heat of combustion can be estimated using data in Reid [14]. The combustion energy per volume is computed from the composition:

$$E_c = W \Sigma (X E_i) \qquad (2)$$

where E_i is the combustion energy of each component per unit weight.

For relative comparison purposes in the data presented below, we assume a use temperature of 24°C (75°F).

The product hazards can be compared from data usually presented in the MSDS if composition of flammable components is stated. Alternatively, the Sax Handbook [15] publishes most of the information on components, except for the Energy of Combustion. If composition of the product is not stated precisely, a modern chemical or environmental laboratory can identify and quantify the volatile components by Gas Chromatography with Mass Spectroscopy.

We define the flammability hazard index for a mixture with the following equation:

$$FHI = [T_a - T_f] E_c V_e \qquad (3)$$

where

T_a = ambient temperature at application, °C or °F
T_f = flash point temperature, °C or °F
    If $T_a < T_f$ the FHI is zero.
E_c = energy of combustion, joules/liter or Btu/gallon of mixture from Eq (2)
V_e = volume of explosive cloud, cubic meters/liter or cubic feet/gallon of mixture from
    Eq (1)

The FHI has an unusual combination of units and it has no specific physical significance. It merely combines the three factors: risk of ignition, energy from ignition and volume of air required for dilution to nonexplosive concentration. A higher flammability hazard index means greater risk of injury by fire or explosion.

A word of caution is appropriate. The specific application and ambient conditions during an incident may be more important than the FHI. At this writing, the authors are involved in litigation where the radiant heat transfer from a hot roof onto an open tray of mineral spirits may have caused sufficient evaporation to reach LEL in a closed garage even though outside ambient air temperature was below the flash point of the mineral spirits.

Table 2 presents the flammable hazard index calculation for a sanding sealer, and Table 3 presents FHI ratings for a number of commercial adhesives and coatings customarily sold in gallon or fractional gallon containers. Many of these are sold for consumer use despite labels stating "For Industrial Use Only." Except for the assumed ambient temperature, these calculations do not involve the usage characteristics of Table 1.

The FHI is appropriate for comparing similar materials. However, for specific accident investigation, the usage conditions of a coating or adhesive can be very important and may show differences not calculated by the FHI. We have tested contact adhesives applied by brush and carpet adhesives applied by trowel. Despite the lower solvent content of the latter mastic (and a lower FHI), its evaporation rate and its rate of explosive cloud formation exceeded that of the contact adhesive. The mastic had more total material per area applied and the multiple ripples from a serrated trowel provided significant evaporation area. Figures 4 and 5 show these relations for two contact cements and for a contact compared with a

TABLE 2—*Combustion energy and flammability hazard index of lacquer #1.*

	Reported Flash Point 0°F, Product Density W = 7.30 lb/gal					
Component	Wt. Fraction in ctg. X	Mol Wt. MW	LEL	Volume of Expl. Cloud cu ft. Eq. (1)	Combustion Energy Btu/lb	Combustion Energy Btu/gal Eq. (2)
Petrol Dist	0.23	100	.012	540	19,300	32,400
Toluene	0.09	92.1	.013	218	17,600	11,600
Isopropanol	0.10	60.1	.020	234	13,150	9,600
Isobutyl Ac	0.21	116.2	.017	300	12,150	18,600
Isobutyl Butyrate	0.05	144.2	.010	96	13,400	4,800
MethEthKet	0.08	72.1	.018	173	13,600	7,900
Sum				V_e = 1561		E_c = 84,900

NOTE: Equation (1) V_e cu ft/gal = Σ (390 $W X$ /LEL MW).
Equation (2) E_c = $W \Sigma$ (X E_i).
Flammability Hazard Index = (75-0) (84,900) (1561) = 9,940,000,000.
Compare FHI of one gallon of gasoline = 27,000,000,000.
Compare FHI of one gallon of rubbing alcohol (70% isopropanol) = 1,500,000,000.

mastic. In this case, the "flammable" mastic (not banned by CPSC) was a greater fire hazard than the "extremely flammable" contact adhesive that was banned by CPSC.

Likewise, a sprayed coating or adhesive will develop a larger explosive cloud faster than a brushed material because of the considerable atomization and evaporation in flight. On the other hand, a bead of construction adhesive from a caulking gun loses its solvent slowly.

To become more application-specific, the V_e, FHI, and TIP (as follows) can all be converted from hazard per volume to hazard per area of surface by dividing the index by the coverage recommended by the manufacturer in units area/volume. Lacquers and sanding sealers are often applied at 7.4 to 12.3 sq m/liter (300 to 500 sq ft/gal); contact adhesives are often applied 2.5 to 6.2 sq m/liter (100 to 250 sq ft/gallon). Troweled mastics may be in the range of 2.5 to 5 sq m/liter (100 to 200 sq ft/gallon).

Likewise, these concepts can be made more application-specific by including measures or estimates of relative evaporation rates and densities of vapor clouds.

TABLE 3—*Flammability hazard indexes of coatings and adhesives.*

Product	Flash Point °F	V_e	E_c	FHI, 10^9
Lacquer #1	0	1510	84,900	9.9
Lacquer #2	20	1790	87,000	8.6
Lacquer #3	37	1540	82,200	4.8
Lacquer #4	57	1660	87,600	2.6
Lacquer #5	20	1810	89,700	8.9
Adhesive #1	−50	1600	81,500	16.3
Adhesive #2	21	1780	62,000	5.9
Adhesive #3	No flash	76	6,330	0
Adhesive #4	−7	874	40,300	2.9
Adhesive #5	−7	1760	86,300	12.3

NOTE: Adhesive #1 is an aerosol spray contact adhesive, maximum package size 24 fl oz.
Adhesive #2 is a flammable contact adhesive.
Adhesive #3 is a chlorinated solvent, nonflammable "rubber" cement.
Adhesive #4 is an extremely flammable construction mastic, applied by spatula.
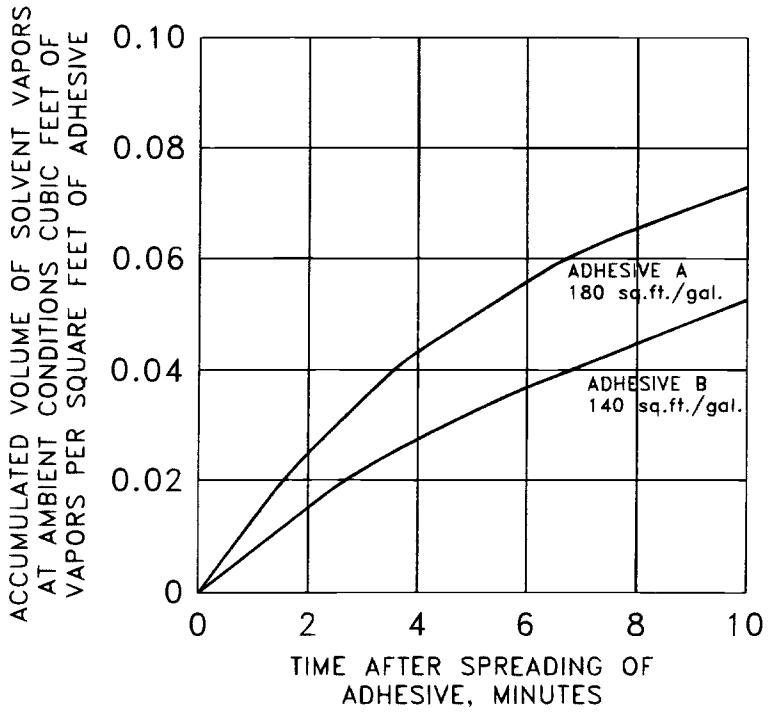Adhesive #5 is an extremely flammable industrial rubber cement.

FIG. 4—*Rates of evaporation of solvent vapors from two contact adhesives when applied at recommended areas. The different solvents had greater effect than the different coverages.*
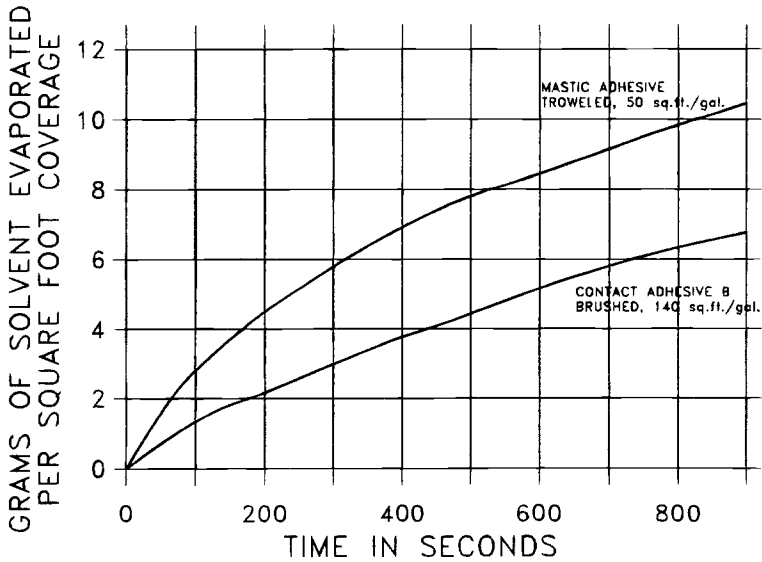

FIG. 5—*Evaporation rates of mastic and contact adhesives.*

Toxic Injury Potential

We combine the factors involved in toxic injury from inhalation of mixed vapors to provide a hazards index with true physical significance. This is the volume of air required to dilute the vapors from one gallon of product to a safe breathing concentration. For each component of the product, the TIP is:

$$\text{TIP cubic meters/liter} = 24.4 \; W \; \Sigma \; (X \, / \, MW \; PEL) \qquad (4)$$
$$\text{TIP, cubic feet/gallon} = 390 \; W \; \Sigma \; (X \, / \, MW \; PEL)$$

where

W = density of the product, gm/ml or lb/gallon
X = weight fraction of the component in the mixture
MW = molecular weight of the component
PEL = Permissible Exposure level of the component (ppm by volume in decimal units, Refs. [8 or 15])

The volume of fresh air required for a mixture of vapors is the sum of the volume required for each component, in accord with OSHA instructions [8].

The calculation of the TIP for a lacquer is presented in Table 4, and comparisons of several lacquers and adhesives are presented in Table 5. A wide range of TIP ventilation requirements are notable. A high TIP may make the user more than tipsy. We were involved in litigation after a painter allegedly became schizophrenic after contact several hours with lacquer #5 (Albert Todd v. QSL Corp et al, 193rd Jud. Dist., Dallas, TX, cause #90-02488L).

The amount of air dilution/ventilation required for safe breathing of vapors can be 50 to more than 100 times the amount of air required to prevent ignition. This comes from a

TABLE 4—*Calculation of toxic injury potential for lacquer #3.*

Component	X	MW	PEL, ppm	X/MW PEL
Naphtha	.25	115	300	7.25
Toluene	.10	92.1	100	10.86
Xylene	.025	106.2	100	2.35
Ethanol	.025	46.1	1000	.54
2-Me Propanol	.15	74.1	50	40.49
Isobutyl Acetate	.15	116.2	150	8.61
		Sum		70.1

NOTE: TIP = 390 × 7.30 lb/gal × 70.1 = 200,000 cu ft/gal = 179 cu meter/liter.

TABLE 5—*Toxic injury potential of lacquers and adhesives.*

Product	TIP, Cu Ft/Gal	Flash point °F
Lacquer #1	208,000	0
Lacquer #2	189,000	20
Lacquer #3	200,000	37
Lacquer #4	81,000	52
Lacquer #5	198,000	20
Adhesive #1	54,000	−50
Adhesive #2	48,000	−7
Adhesive #3	137,000	no flash
Adhesive #4	55,100	−7

comparison of V_c in Table 3 with the TIP of Table 5, both of which are in consistent volume units. The required *rate* of air ventilation is highly dependent upon the application conditions and the rate of solvent evaporation; these are specific to the application.

Conclusions

The concepts of FHI and TIP are of value to the fire investigator, industrial hygienist or toxicologist in relation to specific incidents. They have been basis for testimony by the authors particularly where alternative coatings or adhesives could have been used and injury could have been avoided or mitigated. For example, an inhalation injury was alleged to be caused by lacquer #5 of Table 5 when lacquer #4 could have been used with 2.4 times less TIP (Albert Todd citation as mentioned).

Three of the lacquers and three of the adhesives of this study have been involved in litigation where the authors have expressed persuasive opinions on behalf of plaintiff or defense.

References

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