Handling Industrial Solvents With Safety

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IN handling industrial solvents or working with them, even in the small volumes represented by 10-gallon or 55-gallon drum quantities, it should be remembered that hazards of fire, explosion, asphyxiation, dermatitis, toxicity, or mechanical injury are potentially present and frequently encountered. In fact, such a commonplace material as water, which is the most widely used solvent, can cause damage to property and personnel if improperly or carelessly handled. Although a careless worker may feel that he can afford to take a chance every now and then, the employer or management of a laboratory or plant can not afford to let him take it. This is particularly true in plants or laboratories using solvents because, in such cases, the careless worker not only may endanger himself but also other workmen and the plant itself.

Very few accidents are of the "just happened" variety. Instead, most accidents are set up and result from a chain of circumstances. Makeshift equipment or a lunch basket, a pair of overalls or a box of tools left on a stairway or walkway may set up a simple falling accident, particularly if the makeshift equipment or loose material has an "assist" from poor lighting. For example, a truck delivers a 10-gallon drum of petroleum ether to the loading dock of the laboratory building. Whereupon a chemist, needing some of the solvent in a hurry, comes out and picks up the drum and starts to carry it to the stock room; it is about all he can do to handle the drum, so upon stumbling over a tool box carelessly left along the side of the walkway, he loses his grip thereby letting the heavy drum drop upon his foot. The chemist set up this accident by not taking time to either roll the drum into the laboratory or bring it in on a hand truck that should have been available for handling solvent drums or other heavy objects. Likewise, the one who left the tool box in the walkway helped set up the accident.

Needless to say, a simple but thorough program of safety instruction for all employees handling solvents should be organized and vigorously prosecuted. As Bonotto (1) said "Real instruction—not merely a series of rules—is meant. The superintendent should make frequent examinations to see if the instructions have been thoroughly digested. Danger of explosion (or of toxicity) must be duly emphasized, but not made an object of exaggerated fear, which gives the impression that the man is powerless. The psychological feeling of the worker should be that he is working in a plant having all the safety factors that science is able to produce and that no known danger will come from that end—the only dangerous part of the plant is the worker himself. He must clearly understand that a mistake or a misbehavior of one of them in the extraction building might cause the death of the innocent and that a well understood surveillance of each other will give to each individual worker more assurance of safety." And since the degree of safe practice that is followed by workmen is largely dependent upon the attitude of those in charge, it is important that the management demand strict observance of all safety rules by all employees; having a safety program is quite important, but it cannot be effective unless its provisions are conscientiously adhered to in every day operations by those in charge as well as by the workmen themselves. To illustrate the importance of carrying out instructions, E. B. Free (2) told of an employee who jumped from the top of one cotton oil tank to another, crashing through the top of the second tank to his death, while the superintendent stood there telling him not to jump but to come down and climb up the ladder. Free went on to say, "if you have an employee who will not carry out instructions, you probably will be doing him a favor to let him go." Where the use of solvents is involved, you not only will be doing an unruly or careless employee a favor to let him go but you will be doing the other employees a favor too because one disobeyed safety rule or one careless action on the part of an employee may bring bodily injury to other workmen and mechanical damage to the laboratory or plant.

THE ability to understand safety instructions and to appreciate their importance is a function of general intelligence and education; therefore, insofar as practicable, one should employ men with as much education as possible. Furthermore, the management should be acquainted with an employee's background from the standpoint of integrity, dependability and general health, all of which can be largely ascertained from references, a properly worded application form, and a physical examination, followed by a personal interview of the employee by the superintendent. Then, before the new employee or an old employee who is being transferred to work involving the use of solvents is assigned to a job, he should be thoroughly trained in the company's safety program and in the proper methods of performing the work which he will be called upon to do. It is a good idea to require him to perform his work several times while being watched by the superintendent or foreman to be sure that he understands and does it in the most efficient and safest way. Obviously having a specially selected and trained employee for each task is better than using just anyone who happens to be around. But regardless of how carefully one may select and train an employee for a particular task, sight should not be lost of the fact that various studies have shown certain people to be susceptible to accidents; perhaps they are careless; perhaps they have poor muscular coordination; perhaps they have so many off-duty worries that they are fatigued upon reporting for work; or perhaps they are just unlucky. Whatever the reason may be, any employee with a bad accident record should not be assigned to work involving the use of solvents.

Aside from mechanical injury, such as may result from a workman falling off a ladder or from solvent leaking from a broken line upon stock, possible injury to personnel and plant by solvents revolves principally around the hazards of fire and toxicity

resulting from fairly large amounts of solvent vapors in the laboratory or plant atmosphere. Since solvent vapors of fairly definite concentrations are involved and since most solvents or solvent vapors have a noticeable odor at concentrations far below the lower explosive limit and below the amounts likely to cause irritation or to injure health, the nose usually gives some warning of approaching danger. Allowance has to be made for the olfactory nerves' rapid loss of sensitivity when continuously stimulated by an odor and for the tendency of people to become more and more careless as long time association with a potentially hazardous situation breeds contempt of the danger but, even so, anyone should be alarmed upon entering a room or building to find a strong odor of solvent. If the solvent odor is strong, particularly if it becomes quite strong rather suddenly, the cause should be ascertained as quickly as possible and proper corrective steps taken, both to forestall an accident and to reduce the solvent vapor concentration to normal safe limits. Since it serves as an elementary warning, odor in a solvent is a desirable thing for most laboratory and plant processes from the fire hazard and health hazard standpoints; in fact, if a solvent were odorless, one should carefully consider the possibility of adding to it an odorant or stench material, such as is done in the case of natural gas and liquefied petroleum gas, so that the workmen's nose could at least give some warning of approaching danger.

Tables I and II show some data pertaining to the fire hazard of a number of solvents; Tables III and IV, data pertaining generally to the health hazard of a number of solvents; and Table V, intensity of odor of various solvents. The data and general conclusions in these tables were obtained from K. B. Lehman and F. Flury (3), Morris B. Jacobs (4),

Ibert Mellan (5), N. A. Lange (6), W. C. L. Hemeon (7), Cleaning and Laundry World (8), Occupational Hazards (9), Roy G. Benson and P. M. Van Arsdell (10), John B. Skinner and William M. Pierce (11), Richard B. Pollak (12), W. L. Nelson (13), W. S. Hanna and Robert Matteson (14), Robin Beach (15), Solvents booklet (16), Chlorinated Hydrocarbons booklet (17), Coal-Tar Solvents booklet (18), Joseph J. Matiello (19), Carleton Ellis (20), E. G. Richardson and C. R. Sutton (21), Synthetic Organic Chemicals booklet (22), National Fire Codes (23), and the experiences of the authors.

Investigations into the fields of fire hazard and health hazard of industrial solvents quickly develop wide variations in data and conclusions, the variations in many cases extending to the point of actual conflict. This is not an unexpected state of affairs as one realizes when consideration is given to the fact that the purity and composition of most solvents have varied a great deal over the years and that test methods have not always been on a strictly comparable basis. For example, flash points by the closed cup method ordinarily will be from 10 to 30°F. lower than if determined by the open cup methods, and ignition temperatures may vary as much as 100% by different methods while there is a cloud on some of the toxicity results for the paraffin and naphthene hydrocarbons because many of the "benzine" or "gasoline" samples contained benzene and other aromatic hydrocarbons. Accordingly, in compiling the aforementioned tables, as well as in drawing conclusions relating to fire hazards and health hazard of industrial solvents, efforts were made to weigh the published results and information in the light of various circumstances and to include minimum and maximum values in an effort to provide as complete coverage as practicable.

TABLE I
Some Data Pertaining to Fire Hazard of Various Solvents

Solvent	Distillation Range, °F. Pure	Distillation Range, °F. Commercial	Sp. Gr. of Liquid, Water Equals 1	Sp. Gr. of Gas, Air Equals 1	Auto-Ignition Temperature °F.	Explosive Limits in Air as Percent by Volume Lower Limit	Explosive Limits in Air as Percent by Volume Upper Limit	Tagliabue Closed Cup Flash Point °F.	Remarks About Liquid
	°F.	°F.			°F.	°F.	°F.	°F.	
Acetaldehyde	70		0.783	1.52	365	4.0	57.0	−17	Very Flammable
Acetone	134	132 to 136	0.792	2.0	1,118	2.1	13.0	−4	Very Flammable
n-Amyl Acetate	288	248 to 293	0.879	4.49	714 to 1,046	1.1	......	76	Flammable
Aniline	363	362 to 369	1.022	3.22	1,149 to 1,418	....	......	163	Combustible
n-Butyl Alcohol	243	232 to 245	0.806	2.55	653* to 938	1.7	......	84	Flammable
n-Butyl Acetate	260	234 to 288	0.880	4.00	790 to 841*	1.7	15.0	72	Flammable
Butyl Glycol (Butyl Cellosolve)	340	327 to 360	0.919	4.10	472	....	......	140	Combustible
n-Butyraldehyde	169	160 to 171	0.817	2.48	767	....	......	20	Very Flammable
Carbon Disulphide	114		1.256	2.64	271* to 649	1.0	50.0	−22	Very Flammable
Carbon Tetrachloride	170	167 to 170	1.594	5.32	over 1000	....	......	......	Non-flammable
Chloroform	142	141 to 143	1.489	4.13	over 1000	....	......	......	Non-flammable
Diacetone Alcohol	329	266 to 347	0.931	4.0	1190	....	......	114	Combustible
Dibutyl Phthalate		440 to 455‡	1.047	9.58	757	....	......	322†	Combustible
Diethyl Ether	95		0.710	2.56	366 to 385*	1.2	36.5	−40	Very Flammable
Diethyl Phthalate	576		1.120	7.66	....	....	......	243†	Combustible
Diethylene Oxide (dioxane)	214		1.035	3.03	....	1.9	22.2	65	Flammable
Dimethyl Phthalate		514 to 532	1.190	7.10	....	....	......	269†	Combustible
Ethyl Acetate	171	159 to 173	0.899	3.04	1,016* to 1,130	2.1	11.5	24	Flammable
Ethyl Alcohol	173	169 to 175	0.790	1.59	738* to 1,051	2.3	19.0	55	Flammable
Ethyl Glycol (Cellosolve)	274	259 to 280	0.931	3.10	460 to 715	2.6	15.7	104	Combustible
Ethylene Dibromide	268		2.180	......	....	....	......	......	Non-flammable
Ethylene Dichloride	183	180 to 184	1.253	3.42	775	6.2	15.9	56	Flammable
Formaldehyde (in water)	−6		......	1.03	806	1.3	......	130	Combustible
Furfuraldehyde	322		1.159	3.31	600 to 739	2.1	......	140	Combustible
Methyl Alcohol	147	145 to 150	0.792	1.11	878 to 1,067	5.5	21.0	54	Flammable
Methyl Ethyl Ketone	176	173 to 196	0.805	2.41	960	1.8	11.5	30	Flammable
Nitrobenzene	412		1.200	4.25	924 to 1,033	....	......	190†	Combustible
Nitroethane	237		1.052	2.58	778	....	......	106	Combustible
Perchlor-ethylene	250	249 to 252	1.623	5.83	....	....	......	......	Non-flammable
Phenol	358		1.070	3.24	1,319	1.1	3.3	175†	Combustible
iso-Propyl Alcohol	181		0.789	2.07	852 to 1,173*	2.5	......	53	Flammable
n-Propyl Alcohol	207		0.804	2.07	863* to 1,004	2.2	13.5	59	Flammable
Tetrahydronaphthalene	401		0.975	4.55	....	....	......	176†	Combustible
Trichlor-ethane	188	188 to 190	1.464	4.54	....	....	......	......	Non-flammable

‡ At 37 mm.   * In air from steel surface.   † Cleveland open cup.

TABLE II

Some Data Pertaining to Fire Hazard of Various Hydrocarbon Solvents

Solvent	Distillation Range, °F.		Sp. Gr. of Liquid Water Equals 1	Sp. Gr. of Gas, Air Equals 1	Auto-Ignition Temperature °F.	Explosive Limits in Air as Percent by Volume		Tagliabue Closed Cup Flash Point as °F.	Remarks About Liquid
	Pure	Commercial				Lower Limit	Upper Limit		
	°F.	°F.			°F.	%	%	°F.	
Benzene	176	172 to 248	0.880	2.77	1,076 to 1,213	1.4	9.5	12	Very Flammable
Cycloheptane	244		0.817	3.50	....	....	....	......	Flammable
Cyclohexane	177	175 to 181	0.783	2.91	....	1.3	8.4	2	Very Flammable
Cyclohexene	181		0.810	2.93	....	....	....	......	Very Flammable
Cyclopentane	121		0.753	2.42	....	....	....	......	Very Flammable
n-Decane	345	335 to 360	0.730	4.91	500 to 797	0.6	2.6	115	Combustible
Dipentene	349	338 to 365	0.848	5.7	....	0.8	....	105	Combustible
2-3-Dimethyl Butane (Diisopropyl)	136	124 to 223	0.649	2.97	....	....	....	—20	Very Flammable
2-5-Dimethyl Hexane	229		0.709	3.0	....	....	....	30	Flammable
Ethyl Cyclopentane	217		0.750	3.5	....	....	....	......	Flammable
Gasoline (Paraffinic-Unleaded)	......	95 to 400	0.730	3.5	495 to 550*	1.3	6.0	—50	Very Flammable
n-Heptane	209	194 to 210	0.683	3.46	484* to 843	1.0	6.0	25	Flammable
n-Hexane	156	146 to 156	0.661	2.97	516* to 968	1.2	6.9	—7	Very Flammable
1-Hexene	146		0.678	2.9	....	....	....	—14	Very Flammable
High Flash Naphtha (Aromatic)	......	302 to 392	0.873	3.80	900 to 950	....	....	100 to 110	Combustible
Kerosine	......	355 to 490	0.802	......	490	1.1	6.0	140	Combustible
2-Methyl Pentane	141	130 to 145	0.668	2.97	....	....	....	—17	Very Flammable
3-Methyl Pentane	146	130 to 145	0.673	2.97	....	....	....	—14	Very Flammable
Methyl Cyclopentane	161		0.754	2.91	....	....	....	—5	Very Flammable
2-Methyl Hexane	194		0.701	3.7	....	....	....	20	Flammable
Mineral Spirits	......	302 to 401	0.780	—..	450 to 500	1.1	6.0	103	Combustible
n-Nonane	303		0.718	4.42	450 to 827	0.7	2.9	88	Combustible
n-Octane	258	215 to 264	0.706	3.94	450 to 857	0.8	3.2	56	Flammable
iso-Octane (2-2-4-Trimethyl Pentane)	211	216 to 236	0.692	3.94	1,040	....	....	25	Flammable
n-Pentane	97	88 to 97	0.631	2.48	595* to 1,074	1.4	8.0	—40	Very Flammable
alpha-Pinene	311		0.863	......	....	0.8	....	95	Combustible
iso-Propyl Benzene (Cumene)	307		0.862	4.2	....	....	....	102	Combustible
Petroleum Ether	......	96 to 139	0.636	2.5	579* to 1,053	1.4	5.9	—60	Very Flammable
Rubber Solvent Naphtha	......	130 to 265	0.710	......	495 to 550*	1.2	6.0	—15	Very Flammable
Stoddard Solvent Naphtha	......	308 to 390	0.780	......	450 to 500	1.1	6.0	105	Combustible
Toluene	232	229 to 233	0.866	3.18	1,026 to 1,172	1.2	7.0	40	Flammable
Turpentine	......	295 to 360	0.870	......	488 to 502*	0.8	....	90 to 105	Combustible
VM&P Naphtha	......	200 to 320	0.783	......	450 to 550	1.2	6.0	30	Flammable
o-Xylene	291	275 to 293	0.880	3.66	924 to 1.028	1.0	6.0	63	Flammable

* In air from steel surface.

During university days a good deal of amusement was obtained from the story about the freshman chemistry student saying that "potassium cyanide is so poisonous that a drop of it on the tongue of a dog will kill a man." But when a search is made of the literature relating to solvents toxicity, one finds that much of the data fits this story pretty well; that is, much of the work in toxicological laboratories involves experiments with mice, dogs, rabbits, and so forth, and includes subcutaneous injection and swallowing of the solvents, as well as inhalation and absorption through the skin in the manner of usual workman contacts with the solvents. Results of animal tests are of great value but are not always reliable in judging possible physiological effects of solvents on workmen under practical conditions, as is generally recognized; therefore, regardless of the results of tests on small animals, it seems logical to consider as fairly safe, solvents which have been found to be non-injurious to health for many years under actual working conditions, this being particularly true where there are idiosyncrasies in reactions that result from some workmen being more susceptible or allergic than others. As Lehman and Flury say (3), "the toxic effect of solvents is dependent upon numerous circumstances and, in evaluating dangerousness of the solvents, one must still distinguish between the general theoretically possible toxic effect and the poisoning which is really practical under certain circumstances."

SINCE much of the literature, particularly the older publications, fails to make a sharp distinction between the straight chain hydrocarbons and aromatic hydrocarbons and since many of the commercial petroleum fractions contain benzene, there is considerable uncertainty in some of the experimental results and their evaluation as related to possible health hazards of industrial naphthas consisting principally of paraffin and naphthene type compounds and containing but small percentages, if any, of benzene or other aromatic compounds. For these reasons the probabilities are that toxicity data and industrial poisoning conclusions generally are on the conservative side insofar as the highly refined petroleum naphthas of the paraffin and naphthene type, such as the petroleum ether, hexane, heptane, Stoddard solvent, rubber solvent, lacquer diluent, mineral spirits, and VM&P naphtha fractions are concerned. This certainly seems true when consideration is given to the fact that, aside from temporary dermatitis cases, remarkably few toxicological cases have resulted in industry from the use of petroleum naphthas of the paraffin and naphthene types even though enormous gallonages have been manufactured and used; for example, about 55,000,000 gallons of Stoddard solvent alone are used annually in the United States.

In any event Lehman and Flury (3) point out that "the saturated hydrocarbons are comparatively harmless from the toxicological point of view" and that "if death does not occur very quickly, benzine poisoning almost always is completely cured. After-illness and organic injuries lasting for a rather long period of time have been observed in individual cases, but in most of these cases there is doubt as to their cause actually having been the effect of benzine," and they go on to say that "absorbed benzine is, for the most part, eliminated unchanged from the organism again, the organs of elimination being the lungs and digestive passages." In this connection Jacobs (4) says that "the saturated and unsaturated hydrocarbons of the aliphatic group are relatively harmless from the toxicological point of view, the

lower homologues being less harmful than the higher ones. As a group these substances are not industrial hazards because they are poisonous compounds but rather because they may be present in sufficient quantity to reduce the oxygen content of air in a confined space, such as a tank, below the level which is safe for human beings and because these substances are inflammable and thus are fire and explosive hazards.'' On the other hand, the chlorinated hydrocarbon solvents and the unsaturated cyclic hydrocarbon solvents, particularly those of the aromatic type, are generally recognized as being definitely hazardous from a toxicological standpoint. However, the danger varies largely among the several compounds; for example, tetrachlorethane is much more hazardous than perchlorethylene and benzene is much more hazardous than xylene, particularly in regard to chronic poisoning. In fact, Lehman and Flury (3) report that ''there is great danger of chronic poisoning from trichlorethylene, such symptoms often not appearing for a long time—sometimes after years of work'' and Jacobs (4) said that ''the chlorinated hydrocarbons are among the most poisonous of solvents, being liver and metabolic poisons and having a marked effect on the nervous system and acting as heart depressants.'' He went on to say that ''the aromatic hydrocarbons in general are blood poisons and are much more poisonous than the aliphatic group'' and that ''continued inhalation of turpentine vapors may cause chronic nephritis and a predisposition to pneumonia.''

''The oxygen containing solvents of the alcohol, glycol, ether and alcohol-ether types, as a general rule, are more harmful and poisonous than the aliphatic type solvents,'' according to Jacobs (4) but, ''with the exception of methyl alcohol, the toxicity of the alcohols is comparatively small.'' The oxygen containing solvents of the acid, ester, aldehyde, and ketone types vary a great deal in toxicity and health hazard. As Jacobs (4) points out, ''methyl sulphate is very poisonous but ethyl acetate is almost innocuous,'' and ''the aldehydes rank fairly high in toxicity while the ketones are possibly the least harmful of these groups even though they are markedly stimulating to the respiratory center.''

In general, every substance that dissolves or emulsifies fats has biological effects, if nothing more than acting as a mild skin irritant after repeated exposure. However, for practical laboratory and plant purposes, industrial solvents may be divided as follows:

1. Those solvents which can be considered harmless or which cause no injuries to the workmen's health after long association with them in every-day plant routine. In this group may be placed such comparatively volatile solvents as pentanes, petroleum ether, Stoddard solvent, hexanes, heptanes, rubber solvent naphtha, mineral spirits, ethyl alcohol, ethyl chloride, ethylene dichloride, diethyl ether, diethylene oxide, methyl ethyl ketone, ethyl acetate, and acetone. Also, in this group may be placed certain solvents, which even though considered to be somewhat toxic, are hardly dangerous from a practical standpoint because of their low volatility and usual conditions of use, namely, such solvents as ethylene glycol, dibutyl phthalate, high flash naphtha, butyl glycol, and turpentine.

2. Those solvents which can be considered mildly hazardous or which can be endured by the workmen for a short time within maximum permissible concentrations without serious disturbances or dangerous after-effects. In this group may be placed such solvents as toluene, xylene, cyclohexane, cumene, cycloheptane, propylacetate, amyl

FIG. 1

alcohol, amylacetate, butyl alcohol, trichlorethylene, carbontetrachloride, perchlorethylene, ethyl alcohol, ethylene oxide, hydrogenated cyclic naphthas, tetrahydronaphthalene, and nitroethane.

3. Those solvents which can be considered as definitely hazardous or which cannot be endured by the workmen for even a short time except at extremely small concentrations without possibility of dangerous after-effects or injuring the ability to work. In this group may be placed such highly toxic solvents as benzene, carbon disulphide, methyl chloride, methyl alcohol, tetrachlorethane, formaldehyde, phenol, nitrobenzene, dimethyl sulphate, and pentachlorethane.

It might be said that solvents composed of the paraffin and naphthene hydrocarbons, ethers, primary alcohols, aldehydes, ketones, and certain esters act as general nerve poisons; also, carbon disulphide, trichlorethylene, and similar compounds act as specific nerve poisons. The alcohols have anesthetic and narcotic effects and tend to paralyze the respiratory system, with butyl and amyl alcohols having in addition an irritant action on the mucous membranes and a mild poisonous action on the protoplasm. The secondary alcohols are somewhat stronger narcotics than the primary alcohols. But in general the alcohols, with the exception of methyl alcohol, are among the most harmless industrial solvents. The paraffin hydrocarbons have a narcotic and irritant effect, followed by a paralyzing effect. Physiologically, the cycloparaffins or naphthene hydrocarbons generally show a similarity to the paraffin hydrocarbons. However, the cycloparaffins have a stronger effect; for example, cyclohexane in only one-half the concentration as normal hexane will cause prostration; this same general relationship is true of methyl cyclohexane and methyl hexane. Isoparaffins are less hazardous than the corresponding normal paraffins, and similar toxic pictures are produced by vapors of the olefines, diolefines, acetylenes, and unsaturated naphthenes, such as cyclohexene and cyclohexadien. Hydrocarbons with a branched side chain generally are less toxic than those with a straight side chain. The aldehydes are primarily irritant in action but are fairly high in toxicity and, in common with the ketones and ethers, have a narcotic effect too. In general, the various methyl esters are lung poisons.

The aromatic compounds, particularly benzene and phenol, and the glycols are blood and blood vessel poisons. The glycols and related compounds also act as kidney poisons. The chlorinated hydrocarbons gen-

R.I.P.
HERE LIES THE BONES
OF HARRY JONES,
TO HIM THERE WERE
NO TERRORS.
HE ENTERED AN UN-
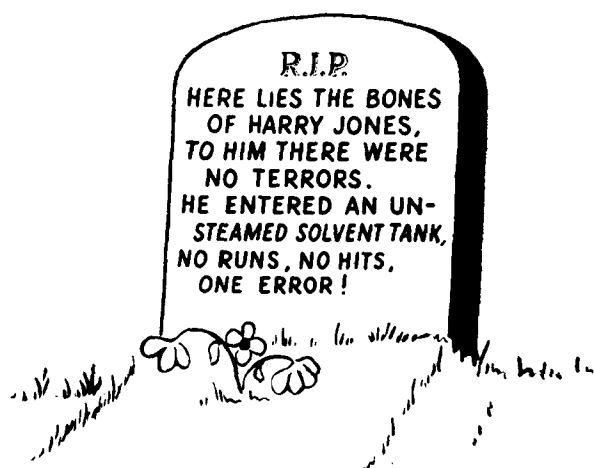STEAMED SOLVENT TANK,
NO RUNS, NO HITS,
ONE ERROR!

FIG. 2

erally act as metabolic, liver and kidney poisons, with tetrachlorethane and pentachlorethane being particularly virulent. In addition, chlorinated hydrocarbon vapors may decompose at high temperatures upon coming into contact with hot metals and flames, with formation of phosgene or other definitely toxic and corrosive substances.

BECAUSE of their volatility and general ability to dissolve fats, practically all industrial solvents, including even the most harmless types, such as ethyl alcohol, acetone, and petroleum paraffin naphthas, are inhalation narcotics and may cause fatal poisoning or suffocation under certain conditions, such as when unmasked workmen enter solvent tanks, or other equipment that has not been sufficiently ventilated. Figures 1 and 2, humorously illustrate what may happen to unmasked workmen who enter solvent equipment that has not been sufficiently ventilated. In fact, the absorption of paraffin and naphthene hydrocarbons or naphthas through the skin is of slight importance so, aside from dermatitis conditions, the absorption of their vapors by inhalation almost exclusively is the cause of the few industrial poisonings in which they have figured. Although absorption of solvents through the skin is not to be overlooked as a source of health hazard, particularly of those types which may decompose into the non-volatile compounds that cannot be eliminated by the lungs or which exhibit secondary toxic effects, such as the action of nitrobenzene, tetraethyl lead, and carbon disulphide, the inhalation of solvent gases ordinarily is by far the greatest health hazard and requires the greatest attention to the end that workmen are not exposed to excessive concentrations, particularly over long periods of time.

Therefore, action should center around measures to prevent or lessen the escape of possibly toxic and inflammable vapors into the laboratory or plant atmosphere and to provide adequate ventilation. Wherever possible, it obviously is better to tighten fittings, replace worn gaskets or packing, change worn shafts, and so forth to reduce the concentration of solvent gases in the laboratory and plant atmosphere than to correct deficiencies of this type by exhaust ventilation; frequently an excessive amount of solvent vapor in the laboratory and plant atmosphere indicates a needless loss of solvent and an unnecessary expense.

But as the old saying goes, "it is indeed an ill wind that blows no good." So it is with the irritant and toxic effects of solvent vapors; that is, flammable or explosive mixtures of the gases in air frequently are practically intolerable to workmen because of the disagreeable or strong odor as well as the irritating action on the eyes, nose, and lungs. Thus, the usually comparatively minor health hazard of combustible solvents frequently serves as a warning that potentially dangerous concentrations of vapors are building up and serve also as a stimulant in getting measures adopted to reduce concentrations of the gas in the room atmosphere to values far below the lower explosive limits. Table V indicates that some solvents, even if highly odorous, may not present a pronounced odor until concentrations are well above the maximum allowable from a health standpoint. Nevertheless, many solvents in the gaseous state not only are sufficiently irritating or obnoxious to cause marked discomfort to workmen at concentrations well below the lower explosive limit but, as is indicated by Tables I, II and VI, may even cause prostration; thus, their health hazard characteristics tend to lessen their fire hazard potentialities.

One of the most amazing effects of hydrocarbon solvents on workmen is the "hydrocarbon jag" which gives many of the manifestations of an ethyl alcohol drunk, such as laughing, uncontrollable muscular actions, dizziness, and general excitement. However, as Benson and Van Arsdell (10) say, "recovery is speedy when the person is removed to open air." Perhaps the most common complaint of workmen handling solvents is that of skin irritation or dermatitis. It is not definitely established whether or not inflammatory skin diseases caused by industrial solvents are a matter of hypersensitivity or allergy to the particular solvent or whether they are a matter of decreased resistance of the skin in a toxicological sense. Perhaps the acute inflammation, resulting from an allergic condition, later takes on a chronic or toxic characteristic. Many consider the skin irritation or dermatitis to be the result simply of the fat-dissolving effect of the solvent, somewhat similar to the chapped condition of the hands that results from excessive washing with ordinary toilet soap, especially in dry, wintry weather. On the other hand, some consider that skin irritation or dermatitis results from some toxic effect of the individual solvents, evidence along this line being that many of the esters and ketones, although good fat solvents, have but little irritating effect on the skin. Be all of that as it may, the hands or other parts of workmen's bodies should not be exposed to liquid solvents or concentrated vapors of solvents any more than is absolutely necessary, and anyone suspected of being especially sensitive or allergic to the solvents should be placed on work which does not require contact with the solvent liquid or vapor. Clothing wet with the solvent should be changed as quickly as practicable, and the wetted parts of the body should be washed with a mild toilet soap followed by application of a healing lotion to restore the oily and pliable condition of the skin. Various ointments and even glycerine, as well as solvent resistant rubber gloves or other protective clothing, help to minimize if not to eliminate skin irritation complaints of workmen coming into contact with solvent liquid or concentrated vapor.

TABLE III
Some Data Pertaining to Possible Health Hazard of Various Solvents

Solvent	Maximum Allowable Concentration of Gas in Air as P.P.M.	For Good Ventilation Concentration of Gas in Air as P.P.M.	Cases of Industrial Poisonings	Possible General Physiological Effects
	ppm	ppm		
Acetaldehyde	100 to 200	25	Few	Damage to lungs and kidneys; marked irritant to mucous membranes; cyanosis; soporific.
Acetone	200 to 420	150	Few	Headaches; irritant to eyes, respiratory tract and skin; narcotic.
n-Amyl Acetate	50 to 400	75	Many	Mildly poisonous; nausea; damage to kidneys; marked irritant to eyes and throat, causing coughing.
n-Amyl Alcohol	56	25	Few	Mildly poisonous; marked irritant, causing coughing and headache; systemic poison.
Aniline	1 to 50	3	Very many	Definitely poisonous; dermatitis; cyanosis; mental confusion; headaches; damage to blood and kidneys.
n-Butyl Alcohol	100 to 200	25	Very few	Mildly poisonous; irritant, causing coughing; dermatitis; damage to blood and liver.
n-Butyl Acetate	47 to 400	75	Very few	Marked irritant to nasal and eye membranes; nausea; narcotic.
n-Butyraldehyde	200 to 400	50	....	Marked irritant to mucous membranes, causing coughing and headaches; nausea.
Carbon Tetrachloride	30 to 100	25	Very many	Definitely poisonous; irritant to eyes, nose and throat; nausea; headache; damages liver and kidneys.
Chloroform	40 to 100	25	Very few	Mildly poisonous; hemolytic; chronic poisoning rare; anesthetic; irritant to mucous membranes.
Butyl Glycol (Butyl Cellosolve)	50 to 400	25	....	Mildly poisonous; irritant to mucous membranes; damage to blood and kidneys.
Carbon Disulphide	3 to 15	3	Very many	Definitely poisonous; narcotic; mental derangement, nervous disorders and blindness.
Diacetone Alcohol	200 to 400	100	....	Damage to liver and kidneys; headaches; irritant to eyes and respiratory tract.
Dibutyl Phthalate	200 to 400	100	None	Irritation of mucous membranes and eyes; dermatitis; danger from inhalation relatively small.
Diethyl Ether	160 to 400	75	Many	Respiratory paralysis; nausea; headaches; loss of appetite; anesthetic; narcotic.
Diethyl Phthalate	200 to 400	100	Few	Gastric disturbances; dermatitis; irritant to eyes; danger from inhalation relatively small.
Diethylene Oxide (Dioxane)	200 to 1,000	25	Many	Definitely poisonous; nausea; narcotic; eye, nose and lung irritant; damage to liver and kidneys.
Ethyl Acetate	140 to 400	75	Few	Damage to blood; irritation of mucous membranes; inflammation of gums.
Ethyl Alcohol	400 to 1,060	250	Many	Digestive and nervous disturbances; narcotic; mental depressant; irritant to mucous membranes.
Ethylene Dibromide	50 to 100	15	....	Definitely poisonous; irritant to eyes and mucous membranes; dermatitis; damage to liver.
Ethylene Dichloride	100 to 200	25	Few	Somewhat poisonous; anesthetic; irritant to eyes and nose; vertigo; hemolytic; damage to kidneys.
Ethyl Glycol (Cellosolve)	50 to 500	50	None	Mildly poisonous; irritant to mucous membranes and eyes; damage to blood and kidneys.
Formaldehyde	20	5	Many	Definitely poisonous; marked irritant to eyes and mucous membranes; dermatitis; protoplasmic poison.
Furfuraldehyde	200 to 1,000	100	None	Irritation of mucous membranes and lungs; nervous disturbances; cramps.
Gasoline (Paraffinic-Unleaded)	500 to 1,500	500	Many	Irritation of mucous membranes; nausea; mildly intoxicating; nervous disorders; dermatitis.
Methyl Alcohol	200 to 380	100	Many	Definitely poisonous; nausea; paralysis and blindness; damage to lungs and nerves; irritant.
Methyl Ethyl Ketone	400	150	....	Marked irritant to eyes and nose; narcotic.
Nitroethane	100 to 200	50	....	Mildly poisonous; irritant to mucous membranes; dermatitis.
Nitrobenzene	1 to 40	5	Many	Definitely poisonous; damages blood; nausea; cyanosis; paralyzes nervous system.
n-Propyl Alcohol	400 to 900	150	Very few	Irritant to mucuous membranes; narcotic; digestive and nervous disturbances.
Perchlor-Ethylene	150 to 200	100	Few	Mildly poisonous; irritant to mucous membranes; narcotic; dermatitis.
Phenol	....	......	Very many	Definitely poisonous; marked lung irritant; dermatitis; damages blood and kidneys; local anesthetic.
iso-Propyl Alcohol	400 to 1,000	150	None	Digestive and nervous disturbances; narcotic; mental depressant; irritant to mucous membranes.
Trichlor-Ethylene	186 to 200	100	Many	Mildly poisonous; narcotic; anesthetic; nausea; irritant to mucous membranes; dermatitis.
Tetrachlor-Ethane	1 to 10	2	Very many	Definitely poisonous; irritant to mucous membranes; damages liver and kidneys; headaches; narcotic.

THE North American National Safety Council (4) in cooperation with its subcommittee on benzol poisonings investigated work rooms in which materials containing solvents were used in the rubber, patent leather, artificial leather, and electrical industries. On the basis of workmen employed in these rooms, a number of whom showed benzene injuries, they reached the conclusion that "the danger of injury to health is not completely removed even with good ventilation equipment which kept the average content of benzene in the air below 100 parts per million." The reason for this probably was because of the fact that in one case the concentration of solvent vapors ran from 30 parts per million minimum to 130 parts per million maximum, even though the average was 90 parts per million, while in another case the minimum and maximum concentrations of solvent vapor in the room atmosphere ran from 0 parts per million to 350 parts per million even though the average was 90 parts per million or a possibly safe concentration.

The comprehensive study by the Pennsylvania Bureau of Industrial Hygiene (8) of solvent exposures in dry cleaning plants of Southwest Pennsylvania is also interesting. This study included 90 plants using petroleum naphthas, a few of which used a mixture of these and chlorinated hydrocarbons, 34 plants using carbon tetrachloride, 22 plants using perchlorethylene, and 10 plants using trichlorethylene. The 90 plants using petroleum naphthas employed 2,965 persons, of whom 211 or 7% were exposed to the solvent, while the 66 plants using chlorinated hydrocarbons employed 453 persons, of

whom 127 or 28% were exposed to the solvents. From the 4,230 samples collected in the 90 plants using petroleum naphthas of the Stoddard solvent and 140-F types, it was found that "the concentration of naphtha vapor in air did not exceed 800 parts per million in any plant or in any operation and that no plant had a greater average than 272 parts per million." From this they concluded that, "if we consider the generally accepted maximum allowable concentration in the range of 500 to 1,000 parts per million for naphtha solvents, these findings clearly indicate on the basis of atmospheric samples that no hazard exists in these plants from the standpoint of inhalation, provided no mixed solvent containing one of the chlorinated hydrocarbons is used." From the 627 samples collected in the 66 plants using chlorinated hydrocarbon solvents, it was found that "of 34 plants using carbon tetrachloride, 7 exceeded 100 parts per million and of these 7, three exceeded 200 parts per million. Of the remaining 27, 10 showed average concentrations between 50 and 100 parts per million and 17 showed concentrations below 50 parts per million," and that "of 22 plants using perchlorethylene, three had an average concentration over 200 parts per million and 19 showed concentrations below 100 parts per million. In the trichlorethylene plants, two out of 10 showed an average exposure exceeding 200 parts per million and 8 were below 100 parts per million."

From this they concluded that, since "the usually accepted maximum allowable concentration for carbon tetrachloride is 100 parts per million and for trichlorethylene and perchlorethylene it is 200 parts per million, these results would indicate that the chlorinated solvent cleaning plant is not operated without danger to health" and that "likewise it is evident that in some cases the operator has been exposed, or has exposed himself to high concentrations of solvent." However, they went on to say that "we firmly believe, despite the findings of some high average exposures, that any cleaning plant can operate with impunity regardless of the present type of machine or solvent used. In this connection we further believe that the most important part of a control program in this industry is the control of the operator's technique. Any program without it will be ineffective."

In considering the foregoing, one is led inescapably to the conclusion that even careful ventilation measures are not complete insurance against dangers to health by industrial solvents, particularly where chronic toxicity is involved. Accordingly, it behooves the management of a laboratory or plant to keep in mind the possibility of replacing solvents which are definitely dangerous to health by less hazardous ones, insofar as practicable.

THE health hazard problem of industrial solvents can be separated into two parts, the one consisting of the relatively easy problem of protecting workmen against exposure to solvent liquid and extremely large concentrations of solvent vapor, and the other consisting of the relatively difficult problem of protecting workmen against exposure to comparatively small concentrations of solvent vapor or gas in the laboratory or plant atmosphere. As already mentioned, workmen ordinarily can be protected against direct exposure to solvent liquid by means of synthetic rubber gloves or by application of glycerine or protective ointments; also, special solvent resistant rubber or plastic hats, suits and boots are available for use in unusually severe situations. In cases of extremely large concentrations of solvent vapor, such as in certain paint spraying operations or the entering of solvent equipment which has not been thoroughly steamed and ventilated, workmen ordinarily can be protected from inhalation of solvent gases by means of a chemical respirator.

Needless to say, an oxygen type mask should not be used where combustible liquids and gases are involved because of the danger of fire and explosion. The fresh air helmet is preferable to other types of gas masks for individual respiratory protection, particularly where compressed air is available; it is especially desirable for use in paint spray booths, in entering solvent tanks or equipment for quick emergency repairs, and so forth. The hose mask, although less comfortable and reliable because of the close-fitting face piece, also is suitable in most similar cases, as is the cannister type mask with activated carbon, alumina or silica gel and other special chemicals. This last mentioned type of mask frees the breathed-in air from solvent vapor by adsorption and by chemical action in certain types, but there always is the possibility that the adsorbent has lost its efficiency and that the concentration of vapors may be above 1.0 to 2.0% or 10,000 to 20,000 parts per million and that oxygen in the air may have been reduced below about 15% to a point insufficient to sustain life. If at all practicable, it is desirable to have a second workman standing by on the outside when it is necessary to send a workman into tanks, operating equipment or buildings in which large amounts of solvent vapors are likely to be present: a pull-rope attached to a workman entering unventilated units also is a worthwhile precaution.

It is worthwhile to encourage workmen in habits of personal cleanliness and to establish a program of frequent medical examinations for workmen coming into contact with solvent liquids or comparatively high concentrations of solvent gases, this being particularly important where even mildly poisonous solvents are involved. Examinations should include blood tests and urinalysis, this being especially true where workmen are exposed to aromatic compounds, halogenated hydrocarbons, carbon disulphide, glycols, methyl esters, and so forth. Regular medical examinations usually enable early symptoms of illness and dermatitis to be recognized and treated while complete and quick recovery is probable. On the other hand, neglected cases may become chronic and even mild dermatitis cases may become more severe and difficult to cure because of secondary infection and aggravation. Early discovery of symptoms of illness on the part of a normal workman may prevent further complaints since it is an indication that leaks have developed in some of the equipment, that ventilation ducts may have become fouled, that workmen are not following the safety rules, and so forth: therefore, the discovery of a case of solvent illness should prompt the superintendent and safety engineer to carefully check the plant operations from both a personnel and equipment standpoint. Likewise, complaints of headaches and dizziness should prompt a careful check, and workmen so complaining should be removed to fresh air; in cases like this, it may be that solvent vapor concentrations are well below that required for

safety but still are too high for worker comfort. In any event, a careful check should be worthwhile.

THE problem of protecting workmen where comparatively small concentrations of solvent gases are involved resolves itself primarily into a matter of adequate ventilation for varnish, paint, lacquer, and ink mixing rooms, rubber cement compounding rooms, drying ovens or closets and rooms, dry cleaning rooms, oil and fat extraction rooms, degreasing rooms, fabric coating rooms, tire fabricating rooms, artificial leather rooms, or other equipment and buildings in which industrial solvent liquids are handled or where the vapors of same may be generated. The solution to the problem appears relatively simple, namely, it is just a matter of providing adequate ventilation; but, as Hamlet said, "aye! there is the rub." Probably the most economical and certain way of providing adequate ventilation, both from a health hazard and a fire hazard standpoint, is to utilize the open air type of plant construction insofar as practicable. The petroleum refining and natural gasoline industries have adopted the open air type of plant construction, similar to that shown in Figure 3, more extensively than any other large industry with the result that fires—especially serious fires and explosions—and toxicity cases have been reduced to a very low figure even though enormous volumes of inflammable liquids and gases are processed under conditions of comparatively high temperatures and pressures. But in spite of the advantages of the open air type of plant construction from the standpoint of economy, health hazard, and fire hazard, the very nature of many types of manufacturing operations as well as comfort of the workmen in northern climates preclude its general adoption to plant construction for most operations utilizing industrial solvents. Therefore, it is necessary in many cases to supplement natural ventilation provided by windows, doors, and louvres with artificial ventilation provided by exhaust fans or other mechanical means. Providing adequate ventilation, however, is not only a matter of equipment and building design supplemented by exhaust fans or other ventilation equipment but also a question of deciding the level of ventilation that is desirable from a comfort standpoint and absolutely necessary from a health hazard standpoint. It is unreasonable to require any piece of equipment or room to be ventilated far below levels shown by toxicological experiments or commercial experience to be adequate for the protection of normally resistant workmen; attention is invited to the "normally resistant workmen" designation, for manifestly it is unreasonable to attempt or to require ventilation of equipment and rooms to a level necessary for workmen who are found to be especially sensitive or allergic to the solvent in question.

Especially sensitive or allergic workmen should be transferred to work which does not bring them into contact with the solvent. This was brought out very well by Lillian Gordon (24) who said "certain individuals are unusually susceptible to the effect of organic solvents. They may be allergic to the liquid so that they develop skin rashes. Or they may be very sensitive to the vapors and become ill under normally safe conditions. This is particularly true of alcoholics and individuals with diabetes, liver damage, or other organic irregularities. If such persons are placed in a solvent-using department, they may become seriously ill even if all the necessary controls are provided and the working conditions are entirely safe for normal individuals. A case of illness, under these circumstances, is not only expensive but most unfortunate from the point of view of the morale of other workers. One 'scare' case of this type has been known to start a wave of panic throughout a large plant." As for that matter, a case or two of this type may start a wave of activity on the part of political units, insurance groups, or unions to require uneconomic operations or unnecessarily expensive ventilation and other equipment in an attempt to doubtfully solve a problem which really would not exist if the extra-sensitive or allergic workman simply were transferred to other tasks which would not bring him into contact with the solvent.
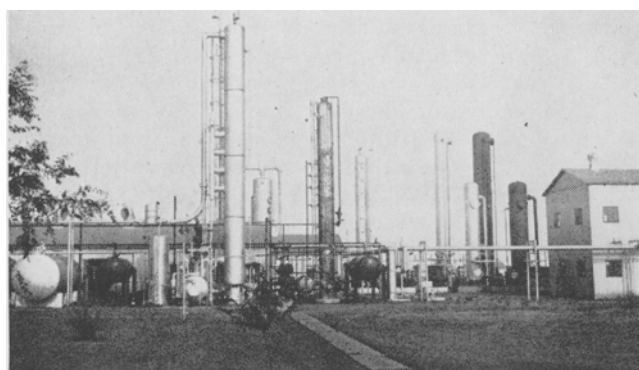

FIG. 3. A Natural Gasoline Refinery.

Along with the allergy cases may be considered the somewhat similar cases of proper living and laxity on the part of workmen. As Gordon said, "personal cleanliness is a vital factor in reducing the incidence of dermatitis" while "a well balanced diet is particularly important in minimizing the possibility of vapor poisoning. Instances may be cited in which workers on a well balanced diet remained well in an atmosphere where others, living mostly on starches or fats, became seriously ill. The drinking of considerable quantities of alcohol, especially the night before, shortly before handling solvents, can make an individual considerably more susceptible to vapor poisoning." But what is adequate ventilation? Obviously, since there are great differences in the irritant and toxic qualities of the various solvents, the ventilation requirements will vary enormously from solvent to solvent. Also, as already indicated, there is considerable variation in toxicological experimental results and doubt in the interpretation of some industrial poisoning cases as well as some question in translating them into practical terms of routine industrial operations. Accordingly, almost any hard and fast rule that anyone might outline would be subjected to serious question sooner or later. In any event, it is reassuring to know that almost any ventilation level that is comfortable and safe from a health hazard standpoint will be relatively safe from a fire hazard standpoint.

THE toxicity data in Table VII from Jacobs (4) illustrate concentrations for various solvents above which, in the absence of other or more compelling data, one dares not permit room atmospheres to go for 30 to 60-minute and 8-hour exposure periods. So,

not taking into account comfort and error factors but allowing for the aforementioned variations and doubts, one might consider the maximum allowable concentrations for vapors of the solvents mentioned to be no higher than the lowest values in the 8 hours exposure column of this table.

In this connection the U. S. Public Health Service and the Army Industrial Hygiene Laboratory, as reported in Occupational Hazards (9), made tests of the chemical content of various products with a view toward indicating their relative danger in cleaning and degreasing operations and indicated that "in general, maximum allowable concentrations have been set variously from 50 to 200 parts per million for the very toxic aromatics and halogenated hydrocarbons, such as benzene, toluene, xylene, carbon tetra-chloride, trichlorethylene, and trichlorbenzene." For the "less toxic groups of alcohols, esters, ethers, and ketones, such as acetone, methyl ethyl ketone, the acetates, and the alcohols, a maximum allowable concentration range of 200 to 400 parts per million permits safety." For the "not particularly toxic paraffins and naphthenes, such as gasoline, petroleum naphtha, Stoddard solvent, the VM&P naphtha, the maximum allowable concentration range was from 500 to 1,000 parts per million."

The Pennsylvania Bureau of Industrial Hygiene, as reported in Cleaning and Laundry World (8), also indicated that the "generally accepted maximum allowable concentration for petroleum naphtha solvents is in the range of 500 to 1,000 parts per million." They indicated the "maximum allowable concentration for carbon tetrachloride is 100 parts per million, while for perchlorethylene and trichlorethylene it is 200 parts per million." The data in Table VIII from Jacobs (4) shows concentration limits that several authorities consider probably safe for various solvent vapors. So, from a careful consideration of the in-

TABLE IV

Some Data Pertaining to Possible Health Hazard of Various Hydrocarbon Solvents

Solvent	Maximum Allowable Concentration of Gas in Air as P.P.M.	For Good Ventilation Concentration of Gas in Air as P.P.M.	Cases of Industrial Poisonings	Possible General Physiological Effects
	ppm	ppm		
Benzene	30 to 100	25	Very many	Definitely poisonous; headache; loss of appetite; irritant; blood damage; dermatitis; narcosis.
Cycloheptane	250 to 800	200	....	Somewhat more toxic than cyclohexane; irritant to mucous membranes; dermatitis; headache; narcotic.
Cyclohexane	500 to 1,450	500	None	At most only half as poisonous as benzene; irritant to mucous membranes; dermatitis; narcotic.
Cyclohexene	500 to 920	250	....	Somewhat more toxic than cyclohexane; irritant to mucous membranes; dermatitis; headache; nausea.
Cyclopentane	500 to 3,750	500	None	Narcotic; irritant to mucous membranes and lungs; dermatitis.
Dipentene	200 to 700	75	Few	Mildly poisonous, causing liver and kidney damage; mucous membranes irritant; dermatitis; headache.
n-Decane	500 to 1,000	500	Very few	Dizziness; dermatitis; irritant to mucous membranes and lungs.
2-3-Dimethyl Butane	500 to 1,000	500	None	Irritant to mucous membranes and lungs; mild dermatitis; intoxicating.
2-5-Dimethyl Hexane	500 to 1,650	500	None	Narcotic; dizziness; dermatitis; irritant to mucous membranes and lungs.
Ethyl Benzene	30 to 200	25	Few	Mildly poisonous, but less hazardous than benzene; dermatitis; irritant to eyes and lungs; vertigo.
Ethyl Cyclopentane	500 to 1,000	500	None	Narcotic; irritant to mucous membranes and lungs; dermatitis.
n-Heptane	500 to 1,000	500	None	Narcotic; dizziness; intoxicating; dermatitis; irritant to mucous membranes and lungs.
n-Hexane	500 to 2,850	500	None	Irritant to mucous membranes and lungs; mild dermatitis; intoxicating.
alpha-Hexene	500 to 2,900	500	....	Dizziness; narcotic; dermatitis; irritant to mucous membranes and lungs.
High Flash Naphtha (Aromatic)	100 to 200	75	Few	Mildly poisonous but much less hazardous than benzene; dermatitis; mucous membranes irritant.
2-Methyl Hexane	500 to 1,250	500	None	Dizziness; narcotic; dermatitis; irritant to mucous membranes and lungs.
2-Methyl Pentane	500 to 3,500	500	None	Irritant to mucous membranes and lungs; mild dermatitis; intoxicating.
3-Methyl Pentane	500 to 3,500	500	None	Irritant to mucous membranes and lungs; mild dermatitis; intoxicating.
Methyl Cyclopentane	500 to 3,500	500	None	Narcotic; irritant to mucous membranes and lungs; dermatitis.
Mineral Spirits (Paraffinic)	500 to 1,500	500	Very few	Dizziness; dermatitis; irritant to mucous membranes and lungs.
n-Nonane	500 to 1,000	500	Very few	Dizziness; dermatitis; irritant to mucous membranes and lungs.
n-Octane	250 to 800	200	Very few	Narcotic; dizziness; dermatitis; irritant to mucous membranes and lungs.
iso-Octane (2-2-4-Trimethyl Pentane)	500 to 1,000	500	Very few	Narcotic; dizziness; dermatitis; irritant to mucous membranes and lungs.
n-Pentane	500 to 8,350	500	None	Anesthetic; intoxicating; irritant to mucous membranes, lungs; mild dermatitis.
alpha-Pinene	200 to 700	75	Few	Mildly poisonous, causing damage to liver and kidneys; irritant to mucous membranes; dermatitis.
Petroleum Ether (Paraffinic)	500 to 7,250	500	None	Anesthetic; irritant to mucous membranes and lungs; mild dermatitis; intoxicating.
iso-Propyl Benzene (Cumene)	30 to 200	25	Few	Mildly poisonous, but less hazardous than benzene; irritant to eyes and lungs; anesthetic; dermatitis.
Rubber Solvent Naphtha (Paraffinic)	500 to 1,500	500	Very few	Dizziness; dermatitis; irritant to mucous membranes and lungs.
Stoddard Solvent (Paraffinic)	500 to 1,500	500	Very few	Dizziness; dermatitis; irritant to mucous membranes and lungs.
Tetrahydronaphthalene	200 to 400	100	....	Mildly poisonous; irritant to mucous membranes; dermatitis.
Toluene	50 to 200	100	Many	Definitely poisonous, but less hazardous than benzene; irritant; damage to blood and nervous system;
Turpentine	200 to 700	75	Many	Mildly poisonous; damage to kidneys and bladder; irritant to eyes, skin and lungs; headache; vertigo
VM&P Naphtha (Paraffinic)	250 to 1,000	200	Few	Dizziness; dermatitis; irritant to mucous membranes and lungs.
o-Xylene	45 to 200	75	Many	Definitely poisonous, but less hazardous than benzene; irritant to mucous membranes and lungs.

formation in Tables V, VI, VII and VIII as well as information from numerous other sources as previously indicated, particularly the discussion on Dilution Rates of Vapors by Hemeon (7) and the textbooks by Lehman and Flury (3), Jacobs (4), and Mellan (5), Tables III and IV were prepared to summarize the possible general physiological effects and general extent of industrial poisonings of various industrial solvents as well as to indicate range of maximum allowable concentration of solvent vapor in air for probable safety over short periods of time and for good ventilation.

The values for "good ventilation" are thought by the authors to be amply conservative from a health hazard or toxicity standpoint since, in line with what Hemeon (7) said, "they are directed not only to the prevention of poisoning but also to the production and maintenance of an atmosphere that will be tolerable and acceptable to the great majority of working people," and, as he went on to say, "at double the values the vapor concentration is still below the maximum allowable required by any state, although quite likely to be objectional." From this viewpoint, as already indicated, many industrial solvents such as amyl acetate, diethyl ether, petroleum naphthas and turpentine, are hardly toxic from a practical plant viewpoint because their vapors are sufficiently irritating or obnoxious that discomfort of the workmen usually results in ventilation to a comparatively safe level.

Solvent vapors ordinarily are heavier than air and tend to collect in low places if ventilation is inadequate but, because of diffusion, convection currents, cross drafts, heating of vapors in drying operations, and so forth, one cannot count upon this too heavily in planning for laboratory or plant ventilation. In fact, Hemeon (7) considers it a fallacy to think that, since solvent vapors are materially heavier than air, this property can be utilized in the design of ventila-

TABLE V

Intensity of Odor in Air of Various Solvents

Solvent	Detectable		Quite Noticeable		Very Strong	
	mg./ cu.ft.	ppm	mg./ cu.ft.	ppm	mg./ cu.ft.	ppm
n-Amyl Acetate....	0.2 to 1.1	1.0 to 7.5	2.0	14	38	258
Amyl Alcohol.......	6.4	63	13	123	61	601
Carbon Tetra-chloride...........	128	733	283	1,580	1,087	6,100
Chloroform..........	93	686	360	2,690	1,321	9,900
Diethyl Ether......	165.1	2,220	423	5,700	1,715	23,100
Ethyl Acetate.......	19.4	190	63	615	191	1,753
Gasoline..............	38.7	300	112	870	400	3,240
Methyl Salicylate.	2.8	16.1	5	29	....	......
Nitrobenzene.......	4.0	33	6.0	49	42	342

tion; also, he emphasizes the inadequacy of "number of air changes per hour" in calculating ventilation requirements and brings out the fact that ventilation requirements should take into consideration the "volumes of vapors formed for given amounts of liquid solvents." As another example of things that may be encountered in maintaining vapor concentration at a given level, Skinner and Pierce (11) mention a case in which "Concentrations of 170 to 230 parts per million of trichlorethylene vapor were found in one metal degreasing plant because of high drafts from adjacent windows whereas concentrations of 30 to 40 parts per million resulted when these drafts were eliminated by baffles."

Aside from some of the halogenated hydrocarbons, such as carbon tetrachloride, perchlorethylene, and trichlorethylene, practically all industrial solvents are combustible, if not highly inflammable, and present more or less of a fire hazard. Even the nonflammable halogenated solvents may complicate fire fighting efforts as a result of decomposing in the flames or in contact with heated metals into phosgene, chlorine or other very irritant and poisonous compounds. But there is some consolation in the fact that hardly any of the industrial solvents undergoes spontaneous combustion, as do rags soaked with linseed

TABLE VI

Minimum Concentration of Vapors Which Caused Prostration (3)

Solvent	Boiling Point °F.	Mg. cu. ft.	Vol. % in Air	Parts per Million
	°F.		%	p.p.m.
Pentane...	97	5,662 to 8,493	8.2	82,000
Hexane...	156	2,831	2.8	28,000
Heptane..	209	1,132	0.98	9,800
2-Methyl Hexane...	195	1,416	1.22	12,200
Octane..	256	991	0.75	7,500
2,5-Dimethyl Hexane..	228	1,982 to 2,265	1.61	16,100
2,7-Dimethyl Octane...	320	......*	......*	......*
Cyclopentane...	131	3,115	3.74	37,400
Methyl Cyclopentane...	162	3,397	3.50	35,000
Ethyl Cyclopentane...	218	1,132	1.00	10,000
Propyl Cyclopentane..	265 to 266	849	0.65	6,500
Cyclohexane...	178	1,416	1.46	14,600
Methyl Cyclohexane..	213	849 to 1,132	0.87	8,700
Dimethyl Cyclohexane (Mixture of isomers).....................	249 to 265	566 to 708	0.49	4,900
Ethyl Cyclohexane...	262	425	0.33	3,300
Pentene (chiefly 3-methyl-b-butene and some b-pentene)........	98 to 101	2,831 to 5,662	5.3	53,000
a-Hexene..	147	2,831	2.9	29,000
a-Heptene...	209	1,699	1.5	15,000
3-Methyl-a,b-butadiene..	105	3,397	4.3	43,000
3-Methyl-a-butine..	85	4,250	5.4	54,000
Cyclohexene...	181	849	0.90	9,000
Cyclohexadiene, (mixture of isomers)...............................	173 to 186	708	0.76	7,600
Benzene...	175	425	0.95	9,500
Toluene...	231	283 to 340	0.26 to 0.32	2,600 to 3,200
Ethyl Benzene..	277	425	0.35	3,500
o-Xylene...	291	425 to 566	0.35 to 0.46	3,500 to 4,600
m-Xylene..	283	283 to 425	0.23 to 0.35	2,300 to 3,500
p-Xylene...	280	283	0.23	2,300
Propyl Benzene..	316	283 to 425	0.20 to 0.31	2,000 to 3,100
Isopropyl Benzene (Cumene)...	308	566	0.41	4,100
p-Methyl Ethyl Benzene..	323	425	0.31	3,100
1,2,4-Trimethyl Benzene (pseudocumene).........................	337	1,132	0.82	8,200
1,3,5-Trimethyl Benzene (mesitylene)...............................	328	708 to 991	0.51 to 0.71	5,100 to 7,100
Butyl Benzene..	356	425	0.27	2,700
p-Diethyl Benzene..	361	849	0.55	5,000
p-Methyl Propyl Benzene..	355 to 356	1,416	0.91	9,100

* Vapor tension too low to cause effect.

oil, rubber latex, soybean press cake, and many other materials; nevertheless, one should not allow solvent wetted clothing, filter cloths, and ordinary rags to lie around haphazardly.

Articles of clothing and usable fabrics that have been wet with solvent should be put in the open air or in special drying closets to dry as promptly as practicable while solvent wetted rags should be put in receptacles provided for them and finally disposed of at the end of each work day. As C. W. Bilbe (25) said in this connection, "it is well to remember that safety and good housekeeping go hand in hand." And as A. Ernest MacGee (26) said, "not to be overlooked is the fact that dust around the plant may present fire and explosion hazards equally as great as that presented by the extraction solvent; therefore, the dust problem in storing, milling, and handling deserves consideration too." In all probability more than one fire or explosion in an industrial plant that has been attributed to the solvent used in the manufacturing operations, has been due to dust generated in the operations or carelessly allowed to accumulate from various sources.

THE fire hazard of industrial solvents should be considered from two points of view, namely, possible damage as a result of "a simple fire" and possible damage as a result of "an explosion."

When a liquid is heated to a temperature at which sufficient vapors are given off so as to be ignited but not to continue to burn, it is at its "flash point." If a liquid is cooler than its flash temperature, it will not catch on fire if a flame is applied to it unless of course the heat of the flame source is sufficiently intense to cause local superheating to the flash temperature; for example, an open beaker of mineral spirits or Stoddard solvent, which has a flash point of about 105°F., will quench the flame of a lighted match slowly inserted into it at a room temperature of about 70°F. On the other hand, a lighted match slowly inserted into an open beaker of VM&P naphtha at room temperature of about 70°F. would cause it to burst into flame since the flash point of VM&P naphtha is about 30°F. In general, the lower the flash point of a solvent, the more likely the liquid is to be set on fire by a lighted match, static spark, hot piece of metal, or other source of intense heat. In the case of simple fires, such as a burning kettle of thinned varnish or tankcar of hexane type naphtha, the combustible liquid is consumed gradually by the flames and burns itself out unless extinguished by fire-fighting measures or unless it happens to spread to other parts of the plant. Therefore, insofar as liquid solvents are concerned, such as in processes of degreasing metal parts by immersion in a vat of solvent, cleaning clothes with a solvent by agitation in a washer, or adding solvent to an open tank of paint ingredients, the fire hazard generally will be greater the lower the flash point and the greater the volatility of the solvent. It should be noted that this type of operation only involves handling the liquid solvent and does not involve distillation of the solvent or evaporation of the solvent in a drying operation. When two or more combustible solvents are mixed, the flash point of the mixture usually will lie somewhere between the lowest and highest flash point of the constituents of the mixture, but sometimes it may be even lower than the flash point of any of the constituents because of the formation of molecular aggregates or azeotropic combinations.

The temperature at which a solvent gas-air mixture takes fire spontaneously is known as the "ignition point," and it may be considered as the lowest temperature at which more heat is generated by the reaction than is lost by radiation and conduction with the result that combustion becomes self-propellent. Ignition point, however, is of only secondary interest from a fire hazard standpoint. It has but little connection with the starting of a fire, and it means that if a solvent already is involved in a fire and temperatures are above its ignition point, the fire may reignite itself even though it had been extinguished by fire fighting efforts. The "fire point" of a solvent is the temperature at which the liquid gives off sufficient vapors to burn continuously upon the application of a flame, this temperature ordinarily being from 40 to 80°F. higher than the flash point of the liquid. Tables I and II show flash, ignition, and distillation temperatures of various industrial solvents. In these tables arbitrary designations of "very flammable," "flammable," and "combustible" are given to solvents with flash points below 20°F., between 20°F. and 80°F., and above 80°F. respectively.

Regardless of how high the flash point or how low the volatility of a combustible solvent may be, it is very inflammable when in the vapor or gaseous state. If the concentration of the gas in air is within certain minimum and maximum limits, the burning proceeds with explosive speed and violence. As one notices from Tables I and II, the explosive limits of solvent gases in air vary considerably from compound to compound but, in general, they are comparatively narrow with the lower explosive limit being in the neighborhood of 1.2% or 12,000 parts per million for the hydrocarbon solvents and 2.5% or 25,000 parts per million for the oxygenated solvents. Thus, an empty or partially empty drum or other piece of solvent equipment is more dangerous than if full of solvent. In a full drum or other piece of solvent equipment the likelihood of an explosion is small because the vapor concentration ordinarily is above the upper explosive limit; so the solvent simply burns if ignited. On the other hand, a freshly emptied or partially empty drum or other piece of solvent equipment, into which a considerable amount of air has been introduced, may have a gaseous mixture that is within the explosive range; if ignition takes place, there may be a shattering explosion instead of a simple fire. Just as "unloaded" guns have resulted in many deaths, many people have been needlessly killed by working on "empty" solvent equipment that had not been steamed and adequately ventilated. The following newspaper (27) account is typical of this type accident: "An explosion of a damaged gasoline tank yesterday morning killed a mechanic, and blew a hole through the roof of a transfer company garage. The mechanic had removed a spare gasoline tank from a truck and was beating dents out of it with a hammer when it exploded, witnesses said. Police said that gasoline fumes apparently had collected in the tank." They might have added that air apparently had collected in the tank too.

As was stated in the Manual of Laboratory Safety (28), one should "think in terms of safe practice constantly and remember that the safe way to accomplish any job is the best way." But in addition, safety

is a matter of cooperation between all concerned; William C. Uhl (29), in reporting on the safety work of R. W. Black and J. E. Jeffries of the Esso Standard Oil Company, summarized it this way: "Safety is teamwork between management and labor, between the foreman and his crew, between operators and maintenance men, between one man and his buddy working alongside of him. It's the company providing the safest equipment and tools available and the employees providing the safest attitude," and he went on to say "statistics tell us that, for every 330 accidents or potential accidents, 300 times no injury happens, 29 times some minor injury occurs, and once a very serious injury or even a fatality pops up." The chance of a serious accident happening is relatively small, and this leads to some workmen "taking a chance" with short cuts or other unsafe practices. However, as already mentioned, the management can not afford to let a workman "take a chance" around a plant using industrial solvents even though the "percentage" chance of serious accident may be small in general gambling terms. Figures 4 and 5 humorously illustrate what may result when a thoughtless or careless workman "takes a chance" around a plant using combustible solvents.

IN taking precautions to prevent solvent explosions, activity should center around preventing the accumulation of solvent vapors, particularly in providing sufficient ventilation to insure that the gas-air concentration is far below the lower explosive limit so that, if fire does occur, explosion will not follow, and around preventing fire from occurring. To prevent accumulation of solvent vapors, open type construction may be followed wherever practicable and, where closed type construction is used, plans for adequate ventilation should be adopted wherever necessary; adequate ventilation is desirable from a health hazard standpoint and, as already mentioned, when concentration of solvent vapors in the room atmosphere is kept low enough from the standpoint of comfort and health of the workmen, it will be below

the lower explosive limit in nearly all cases. It is desirable to incorporate in the buildings a relatively large window area, since windows let in light and assist in ventilation, especially during an emergency, such as when a solvent line breaks or a tank is overflowed resulting in overloading the exhaust fans or other ventilation system with a surge of solvent vapor. In plant operations which only involve handling of the liquid solvent and do not involve atomization or distillation of the solvent or evaporation of the solvent in a drying operation, such as in processes of degreasing metal parts by immersion in a vat of solvent, cleaning clothes with a solvent by agitation in a washer, or adding solvent to an open tank of paint ingredients, the tendency to accumulate vapors in the room atmosphere generally is reduced the lower the volatility, vapor pressure, and boiling range and the higher the flash point of the solvent. However, in plant operations which involve atomization or distillation of the solvent or evaporation of the solvent in a drying operation, such as in paint spraying, cottonseed oil extraction, and fabric coating processes, there is little, if any practical difference in the fire hazard of the several combustible solvents from which selections ordinarily would be made, regardless of the flash point, vapor pressure, volatility, and boiling range. This follows from the fact that all of the solvents in the vapor or gaseous state are highly inflammable and may form explosive mixtures with air as well as the fact that the operation involves converting the liquid solvent into the vapor or gaseous state; therefore, there is little difference in the fire hazard of a cottonseed solvent extraction plant regardless of whether butyl alcohol, ethyl alcohol, VM&P naphtha, heptane, or hexane be used. The flash point of n-butyl alcohol is 84°F., while it is 55°F. for ethyl alcohol, 30°F. for VM&P naphtha, 25°F. for n-heptane, and -7°F. for n-hexane, but the vapor of the one is just as inflammable as the vapors of the others for all practical purposes. As a matter of fact, under certain conditions in "vaporizing" operations of this kind, the higher flash point solvents may present the greater

TABLE VII

Toxicity Data on Various Solvent Gases in Air (4)

Solvent	Dangerous to Life in 30 to 60 Minutes		Maximum for 60 Minutes Without Serious Disturbance		Slight Symptoms After 8 Hours' Exposure	
	Milligrams per cubic foot	Parts per Million	Milligrams per cubic foot	Parts per Million	Milligrams per cubic foot	Parts per Million
Acetone	651 to 3,255	10,000 to 50,000	....	....	....	....
Acrylic Aldehyde	9.9 to 15.6	153 to 240	....	....	....	....
iso-Amyl Acetate	....	....	781 to 1,562	5,000 to 10,000	....	....
sec-Amyl Acetate	....	....	838	5,000	300	2,000
Aniline	....	....	11.3 to 17.1	100 to 160	0.85 to 5.7	7 to 53
Benzene	707	7,500	283 to 425	3,000 to 4,700	141 to 283	1,500 to 3,000
Benzine	1,245 to 2,490	11,000 to 22,000	538 to 991	4,300 to 7,100	141 to 283	1,200 to 2,500
Butyl Acetate	1,507 to 2,108	10,000 to 14,000	1,060	7,000	495	3,300
Carbon disulphide	85 to 349	1,000 to 3,850	42.5 to 141	480 to 1,600	28.3 to 34	300 to 390
Coal Tar Naphtha (Aromatic)	707	7,500	283 to 425	3,000 to 4,700	141 to 283	1,500 to 3,000
Carbon Tetrachloride	4,240 to 5,660	24,000 to 32,000	1,698 to 2,263	4,000 to 13,000	283	1,600
Cellosolve (Ethyl Glycol)	....	....	....	....	104.8	1,000
Chloroform	849 to 2,120	6,100 to 15,000	707 to 848	5,000 to 6,000	283 to 849	2,000 to 6,000
Diethylene Oxide (Dioxane)	1,443 to 2,890	15,000 to 30,000	396 to 509	4,000 to 5,000	209 to 289	2,000 to 3,000
Ethyl Acetate	1,019 to 2,038	10,000 to 20,000	....	....	....	....
Ethyl Alcohol	....	....	473	8,000	53.8	1,000
Ethyl Bromide	1,261 to 2,525	10,000 to 20,000	758	6,000	215 to 379	1,700 to 3,000
Ethyl Chloride	4,470 to 7,470	60,000 to 100,000	3,000	40,000	1,472	20,000
Ethylene Dichloride	331 to 495	4,000 to 6,000	289	3,500	82.1	1,000
Ethylene Oxide	153 to 306	3,000 to 6,000	153	3,000	12.7	250
Diethyl Ether	2,970	35,000	....	....	....	....
Formaldehyde	....	....	....	....	0.7	20
Gasoline (Paraffinic-Unleaded)	1,245 to 2,490	11,000 to 22,000	538 to 991	4,300 to 7,100	141 to 283	1,200 to 2,500
Heptane	1,245 to 2,490	11,000 to 22,000	538 to 991	4,300 to 7,100	141 to 283	1,200 to 2,500
Methyl Alcohol	1,838	50,000	....	....	....	....
Methylbutyl Ketone	1,159 to 2,318	10,000 to 20,000	348	3,000	116	1,000
Methylethyl Ketone	4,530 to 9,060	50,000 to 100,000	906	10,000	272	3,000
Nitrobenzene	....	....	28.3	200	5.6 to 11.3	40 to 80
Toluene	707	7,500	283 to 425	3,000 to 4,700	141 to 283	1,500 to 3,000
Trichlorethylene	....	....	....	....	....	....
Xylene	707	7,500	283 to 425	3,000 to 4,700	141 to 283	1,500 to 3,000

GEE BUT ITS DARK TONIGHT. MY LANTERN SURE COMES IN HANDY

FIG. 4

MY CHEMIST RUNS A SOLVENT-OIL STILL. MY CHEMIST WORKS BY THE BLUE SEA. WITH A LANTERN HE WENT TO THE MILL. OH, BLOW BACK MY CHEMIST TO ME.

FIG. 5

fire hazard because of the hotter liquid and vapor as a result of the higher boiling range and lower volatility. Certainly, there is no justification for a statement made in connection with Eriez non-electric magnets (30) to the effect that "solvent extraction presents a terrific hazard of fire because of the use of paraffin solvents—which are more volatile and explosive than gasolines." On the contrary, the paraffin solvents used so extensively in the vegetable and animal oil extraction industry are, if anything, less hazardous than ordinary motor gasoline because of the absence of extremely volatile compounds, such as butanes and iso-pentanes.

Gasoline, even though it has an end point of about 400°F., has a high percentage of comparatively low boiling compounds, as is evident from the fact that it has a flash point of about -50°F. and an initial boiling point of about 95°F.; also the vapor pressure of gasoline varies with the season generally from about 8 to 13 pounds per square inch at 100°F. The hexane and heptane type petroleum naphthas, which are the "paraffin solvents"alluded to, have flash points of about —20 and 20°F., respectively. The hexane type naphtha has a general boiling range of 146 to 156°F. while the general boiling range of the heptane type naphtha is 194 to 210°F.; although they have much lower end points and smaller amounts of comparatively high boiling compounds, their distillation range is much closer and they have much less comparatively low boiling or extremely volatile compounds than gasoline has. This is evident from their comparatively low vapor pressures, that of the hexane type naphtha being about 5.1 pounds at 100°F. and that of the heptane type naphtha being about 2.1 pounds at 100°F. As Bilbe (25) so aptly put it, "although much has been said regarding safety measures for a solvent extraction plant, it is well not to lose one's perspective about the degree of hazard entertained in the operation of such a plant. Properly installed and operated, the risk is not as great as that encountered in a filling station or bulk station handling motor fuel."

In this connection it is interesting to note that in the same issue of the journal, in which was made the aforementioned statement about "solvent extraction presenting a terrific hazard of fire," there was a report of fire raging through a soybean oil mill and causing damage of about $900,000. The Oil Mill Gazetteer (31) reported as follows: "The fire 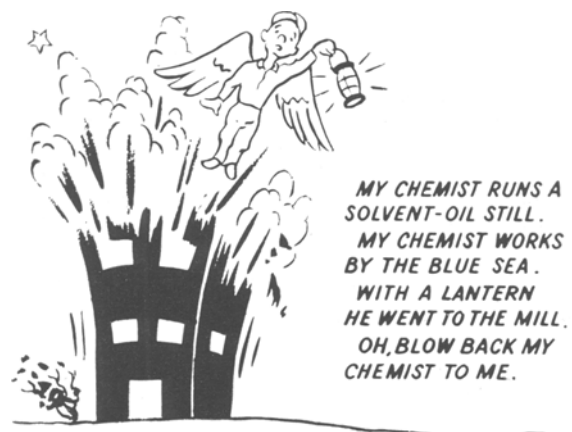broke out in the center of the operations plant less than 10 minutes after the company's night watchman had punched his clock there. The watchman said the fire seemed to just 'flare up' and spread almost at once throughout the building." This was a report of an oil mill which did not use the solvent extraction process, and yet it was a fire which "seemed to flare up and spread almost at once throughout the building." Perhaps it was a dust fire essentially, or it might have originated from spontaneous combustion of oil bearing material and have been aggravated by dust. Or, consider the case of an "earth-shaking" explosion that occurred at a solvent extraction plant. As reported in the newspaper (32), "the blast shattered the roof of the one-story sheet metal building, and fire department officials estimated the damage at $12,000. The blast left the boiler room in ruins and blew out the top of the main boiler. The engineer said that the explosion might have been the result of unfired gas fumes which built up in the boiler's fire box and were ignited by hot bricks or delayed firing of the pilot light." The part of the plant in which extraction solvents was utilized was not damaged. In any event, these cases chosen at random forcefully illustrate the fact that, although combustible solvents are a fire hazard, industrial plants can and do burn—burn with explosive violence where many dusts are involved—under circumstances wholly unrelated to any solvent. Therefore, safe practices should be followed throughout the entire laboratory or plant as well as in those parts of it in which solvents are used; particular attention should be given to preventing the accumulation of solvent vapors or other gases and combustible dusts.

IN a properly designed, ventilated, and operated plant, the chance of a fire is small indeed if all flame or intense heat that might start it is kept away. Almost needless to say, such sources of flame and sparks as ordinary lanterns, cigarette smoking, lighted matches, blow torches, open electric lights and switches, non-explosion proof motors, metal welding and cutting operations, and hammering of metal equipment should be kept away or tolerated only wherever necessary around the laboratory or plant, and then only after the superintendent or safety engineer has determined that solvent vapors either are absent or are present in concentrations well below the lower explosive limit. Both portable and stationary, continuous types of apparatus are available for use in quickly testing gas-air concentrations at any de-

TABLE VIII
Probable Safe Concentration Limits of Exposure for Gases in Air (4)

Solvent	State of California		State of Massachusetts		Dalla Valle		Flury	
	mg./cu. ft.	ppm	mg./cu. ft.	ppm	mg./cu. ft.	ppm	mg./cu. ft.	ppm
Acetone	14.7	200	......	......	......	......	......	422
iso-Amyl Acetate	65.7	400	65.7	400	147.2	900	7.1	47
Amyl Alcohol	......	......	......	......	......	......	5.7	56
Aniline	0.3	2.5	......	5	0.6	7	......	....
Benzene	9.6	100	7.1	75	9.6	100	2.8	31
Benzine (Gasoline, Heptane)	113	1,000	113	1,000	170	1,500	28	250
Butanol	9.3	100	......	......	......	......	9.3	100
Butyl Acetate	59.5	400	59.5	400	1,084	7,200	7.1	47
Carbon Disulphide	0.1	1.0	1.4	15	7.1	85	0.3	3
Carbon Tetrachloride	19.5	100	19.5	100	19.5	100	5.7	32
Chloroform	15	100	......	......	......	......	5.7	40
Diethylene Oxide (Dioxane)	......	......	......	......	102	1,000	......	....
Ethyl Acetate	......	......	......	......	......	......	14.2	130
Ethyl Alcohol	14.2	250	......	......	57	1,000	59.2	1,064
Ethyl Glycol (Cellosolve)	......	......	......	......	51	500	......	......
Ethylbenzene					122	1,000	......	......
Ethylene Dichloride	122	100	122	100	1,217	1,000	5.7	494
Ethyl Ether	36.8	400	36.8	400	......	......	14.2	165
Formaldehyde	0.7	20	0.7	20	0.7	20	......	......
Methyl Alcohol	4	100	7.9	200	4.	100	14.2	382
Methyl Bromide	......	......	......	......	1.4	100	......	......
Methyl Chloride	31.1	500	......	......	73.6	1,200	14.2	242
Methylethylketone	......	......	......	......	252	3,000	......	......
Monochlorbenzene	10.5	75	10.5	75	......	......	0.4	2
Nitrobenzene	0.2	1.0	1.0	5	9.3	60	......	......
Perchlorethylene	41.9	200	41.9	200	20.9	100	28.3	147
Propyl Acetate	......	......	......	......	......	......	70.8	83
Tetrachlorethane	2.1	10	2.1	10	......	......	......	......
Toluene	11.9	100	23.8	200	......	......	5.7	53
Trichlorethylene	31.1	200	31.1	200	15.6	100	28.3	186
Turpentine	113.2	700	36.8	200	115	720	......	......
Xylene	13.6	100	27.2	200	13.6	100	......	......

sired point around the plant; but if such equipment is used, a chemist or instrument man should check it periodically to be sure that it is functioning properly.

Spark-proof tools should be used in making repairs wherever practicable. Spark-proof shoes are recommended, but rubber shoes should not be worn by workmen unless they are made of "conducting" rubber. Hot sparks or cinders from coal-burning locomotives and from trash burners or even from grass fires are a remote but possible cause of fires so they should be kept in mind when considering a safety program.

All electrical equipment and wiring is a potential fire hazard because of occasional generation of intense heat, due to overloading, as well as sparks. Lights should have explosion proof globes that also are shielded to protect against mechanical breakage; unshielded lights should never be used around solvent equipment or in rooms where combustible gases or dusts may be present because they might be broken by contact with something, thereby permitting their hot wires to light off a fire or explosion. Periodic checks should be made by the safety engineer or an electrical engineer to be sure that circuits are not overloaded, that motors are not heating unduly, that insulation has not deteriorated, that connections are not faulty, and that wiring has not become threadbare. By all means do not allow a motor which has had solvent spilled on it continue to run, and don't use makeshift electrical hook-ups. Switches and motors, insofar as practicable, should be of the explosion proof types and preferably installed outside drying equipment or other rooms in which appreciable quantities of combustible solvents or dusts are likely to be encountered. Multiple sockets are to be avoided wherever practicable.

Of all the sources of fire and explosion, the static or friction spark undoubtedly is the most insidious. It is difficult to control and, unless controlled completely, is likely to strike without warning at any time. As pointed out by E. E. Turkington (33), "rubber cement coating and spreading processes always have been plagued by relatively frequent fires,

the peak having been reached during the war with greatly increased use of the processes in working reclaim and synthetic rubber. Almost all of the fires—97% of them—are caused by static electricity. You can't prevent the generation of static electricity. It is produced by the moving parts of machinery, by the fabric, and by the rubber cement. Since combustible thinner vapors are always present (regardless of the amount of artificial ventilation) at rubber cement dip tanks, at doctor knives, and at the surface of freshly coated fabric, static sparks should be prevented in the vicinity of a rubber spreading machine and, in fact, at any place where rubber cement is used. It is, consequently, of first importance to ground the frames of all machines at which rubber cement is used, including all metal rolls, metal parts of reels, and rubber receptacles. Rolls and rotating shafts are often found to be insulated by lubricating oil or grease. Metal hoppers and cement receptacles may be insulated from the machine frame by paint, corrosion, or cement. Rolls and rotating parts should, therefore, be grounded by means of spring-brass or carbon brushes and all insulated or isolated metal parts should be bonded to the frame of the machine or separately grounded. A No. 4 stranded copper conductor is advised. The ground wire should be connected to a permanent ground such as a sprinkler or other water pipe. Buried plates or driven pipes or rods are acceptable if water pipes are not available but should be tested periodically so that any impairment will be detected. Static is generated at the point where fabric is unwound from the roll at the feed end of a coating machine and at every roll over which the fabric passes. The grounded collector brush should be installed about four inches in the direction of travel from the roll which causes the static, and the ends of the bristles should be between ¼-inch and 1-inch from the surface of the fabric. Contact with the surface is not necessary." Turkington's article has been quoted at some length because his suggestions generally are applicable to many other operations, such as solvent extraction of vegetable and animal oils, grinding of extracted meals, continuous painting processes, con-

tinuous drying processes, travel of materials through conveyors, and so forth.

The movement of the solvent itself through pipes and other equipment may create sufficient static electricity to cause a spark under certain conditions, such as in transferring solvent into another container, and thereby start a fire. In flowing through pipe, the solvent generally tends to acquire negative electricity while the piping tends to acquire positive electricity which ordinarily is eliminated by its ground. As the negatively charged solvent flows from the pipe into a drum, tank, or other ungrounded piece of equipment, the potential of the receptacle increases until a point may be reached at which a spark discharge results. But if the drum, tank, mixing machine, or piece of equipment is grounded, the electrical charge of the moving solvent is transferred to the equipment and dissipated through its ground. Therefore, equipment or receptacles into which any appreciable quantity of solvent is to be poured should be adequately grounded as well as the units from which it is to flow.

ALTHOUGH it is a relatively minor problem in most operations, the fact that workmen through body electrification may create a fire hazard should not be overlooked. It is possible for workmen to acquire an electric potential by walking upon insulated flooring or wearing shoes with non-conducting soles, by touching charged containers or equipment, and by handling charged materials, such as rubber stock, fabrics, and feedstuffs, this being especially so in dry, wintry weather. As Robin Beach (15) puts it, "individuals differ widely as to their characteristics of skin resistance, and occasionally a person is found who possesses such a deficiency in the proper functioning of the sweat glands that the skin resistance of the feet, which should not normally be in excess of $\frac{1}{2}$ megohm, may be found greatly in excess of this value. A person of this type in a plant is sometimes found to be responsible for most of the electrostatic fires which occur in a given type of processing— whence comes the dubbed cognomen to these individuals of 'hot mammas' or 'hot papas'." In this connection Rollin H. Wampler (34) mentions the case of a "paint plant being totally destroyed by fire resulting when a workman leaned over to pick up an open pail of lacquer thinner. The static charge built up on his body leaped to the pail and caused the solvent to ignite." In view of this workmen should wear shoes with conducting soles, and flooring should be of the conducting type and well grounded, particularly around fabric coating units, mixing machines, oil extraction units, paint spraying booths, or other areas where relatively large amounts of solvent vapors are to be expected. As for that matter, a workman suspected of being unusually "hot" electrically should be transferred to work where he would not come into contact with combustible solvents and dusts.

It is well known that static electricity becomes more of a problem in dry, wintry weather and in heated buildings where humidity is likely to be low and that fires resulting from it are much less during the comparatively humid summer months. One's memory of the possibilities of static electricity often is refreshed upon touching a door knob or an elevator button, after walking on a carpet during dry wintry weather; not only does one under these circumstances receive a mild shock, but visible and audible static sparks

are released. Although it is not absolute protection, high humidity largely prevents the accumulation of static charges on non-conducting materials and equipment as well as on conducting materials and equipment that are not properly grounded. Under conditions of high humidity a film of water forms on the surface of non-conducting materials and equipment, rendering them somewhat conductive, thereby enabling the static electricity to be slowly discharged to the ground as well as to the humid atmosphere. Maintaining a comparatively high humidity of, say, 60% may not be practicable in many cases because of deleterious effects on the materials being processed, cost of humidity control, comfort of workmen, and so forth. However, it is well to bear in mind that moistening materials to be handled, ground, or mixed and maintaining high humidity in the room atmosphere tend to reduce the fire hazards resulting from static electricity so consideration should be given to their utilization wherever practicable if large amounts of combustible gases or dusts are expected to be encountered.

J. R. O'Hanlon (35) commented, in discussing fire prevention in drycleaning plants, "if your tumbler is not equipped with steam jet, install a line to the air inlet and allow a small amount of steam to enter with the air. This will prevent static and help remove lint from garments. Steam is one of the best methods of smothering fires in closed equipment. Every tumbler, dry room, or cabinet should be equipped with a steam line with automatic or hand valve for this purpose."

Without attempting to discuss from a fire hazard standpoint the details of building design and plant layout, which vary enormously in the several industries using solvents as well as from plant to plant in the same industry because of local circumstances, it might be said generally that wherever open type construction is not considered practicable enclosing walls should be of light construction, with non-combustible materials, and provided with ample window area, to serve as a pressure release in case of an explosion. Large window area serves also to let light into the plant and facilitates ventilation when surges of solvent vapors are released within the plant or when exhaust fans or other ventilating equipment breaks down. Above ground floors and stairs should be of the grill or open type insofar as practicable to lessen the chance of pockets into which liquids or vapors may collect. Bonotto (1), in discussing the desirability of having the solvent extraction building limited to the "steel frame supporting the processing equipment, with siding and roof of light sheet metal," made the observation that "such a mass of metal, well bonded and grounded, will act also as a protection against lightning, as demonstrated in a plant in Evansville, Ind., which in 1934 during full operation, with all men inside, was struck by lightning without any disturbance at all."

Care must be taken to the end that hallways, conveyors, spouting or other ducts do not permit solvent vapors to escape from the solvent processing rooms to other parts of the plant and thereby set up a health and fire hazard in areas where suitable precautions ordinarily would not be taken. Wherever possible, special solvent processing equipment should be sealed, enclosed, or provided with some type of hood so as to lessen the escape of solvent vapors into the general room atmosphere. It makes for shipshape appearance

and lessens chance of confusion if solvent piping, pumps, and operating equipment are painted a distinctive color—red, for example—several different colors being used if solvents of different type or specification are used. It is a good idea to use welded assemblies as much as possible in order to reduce possibility of leaks at pipe joints; flanged connections and valves should be used only when there is definite need for them, as they are sources of solvent leaks, and one should make sure that they are bonded by copper braid, sprayed zinc, or other metal contact to maintain integrity of electric conductance to the ground. Ample capacity drains, of course, should be provided wherever solvent is likely to be spilled in quantity so that the liquid readily can be removed from the room where it may create health and fire hazards.

It is well to consider "fireproofing" I-beam legs or other metal supports for tanks and processing equipment containing large amounts of solvent in order to lessen the chance of collapse in case of fire, which may break open the equipment or spill the solvent, thereby aggravating the fire. To fireproof structural steel with concrete, the mortar, composed of 1 part Portland cement and 2 parts sand, is poured into a form surrounding the steel leg or stanchion which first has been given one wrap with concrete reinforcing wire mesh. Other materials may be used, such as brick, magnesia insulation with galvanized covering, and so forth.

NO discussion of handling solvents with safety would be complete without at least a few words about storage facilities. If the solvent comes into the plant in drums, the problem is simplified in the beginning since special storage tanks, piping, pumping, and tank truck or tank car unloading facilities do not have to be provided. Nevertheless, the handling of solvent in drums is a multiple hazard which requires continuous vigilance. In the long run, tank storage not only is more economical but probably is less hazardous if comparatively large volumes of solvent are handled. The superintendent or safety engineer should satisfy himself that the drums are of a proper type for handling the particular solvent and he should be certain that no solvent can leak from the bungs or seams. If a drum is leaking at the seams, its contents should be emptied promptly; if the drum is leaking at the bungs, which frequently may be the case since the plugs may be loosened in transit, the fault usually can be corrected by simply tightening the plugs or by installing a new gasket. To test for leaks the drums should be laid on their sides; however, when in stock rooms the drums should be set head up so that liquid solvent will not escape even though leaks may develop at the plugs. However, if drums are to be stored outside where rain or snow may fall on them, it is recommended that they be set on their sides since water accumulating on the heads may be sucked into the drums, thereby contaminating the solvent. Drums with both bungs or openings in the head are preferable to those with a side bung from a fire hazard standpoint. When unloading and handling drums, take care not to drop them—drums should be rolled or preferably moved around the plant on hand trucks or small mechanical trucks.

As soon as one has finished pouring liquid from a drum, insert and tighten the plugs at once to prevent creating a needless fire hazard by possible loss of liquid and vapor. When drums have been emptied, they should be taken back to their regular storage place and returned to the solvent supplier as soon as practicable. An empty solvent drum is still a fire and explosion hazard if it contained a combustible solvent. Drum storage rooms should be adequately ventilated to avoid possible accumulation of vapors and usual safety precautions taken; facilities should be provided for draining away solvent which may leak or spill from the drums in large amount. The drums should be stored in a building away from the other plant buildings, if possible, or in a room which is separated by a fire wall from the other plant activities. Each drum should be plainly labeled or tagged as to contents and safety precautions to observe so that workmen cannot confuse one material for another or be ignorant of the hazard presented by the drum's contents. Drums containing inflammable solvents should be painted red since red is generally recognized as a danger color.

It is recognized that there are good arguments for below ground solvent storage tanks, and that some insurance and local fire officials recommend below ground installations to above ground installations. Nonetheless, below ground level storage is never recommended by the authors where it is practicable to install above ground tanks. Above ground tanks are more easily inspected, cleaned, and kept in repair and, if properly diked and located away from other buildings, present no unusual fire hazard even where the more volatile and inflammable solvents are handled. In fact, it frequently happens that the solvent storage, whether above or below ground, is less hazardous from both a fire and explosion standpoint than other parts of an industrial plant in which solvents or combustible dusts are encountered. Unless it is securely fastened, there always is the chance that a below ground tank may be floated during periods of extremely wet weather or overflow of streams, thereby breaking connections and creating a fire hazard. Also, underground tanks tend to become leaky as a result of corrosion and strain. Underground leaks ordinarily are slow to be detected, during which time seepage may take the solvent far afield to produce a fire hazard at any unexpected place. The following newspaper (36) report taken at random is of interest in showing the possible seriousness of underground leaks: "A week-long search for the source of subterranean gasoline flow that caused a pocket in the basement of a downtown ten-cent store ended Saturday with the removal of a 550-gallon storage tank near the establishment, the fire marshal reported. The fire marshal located the gas pocket in the store Monday and warned occupants of the building in the immediate area that gas fumes might be present and that an explosion could occur. The owner of the oil company said, when pressure was applied in a test, two holes were discovered in the tank."

Tanks should be equipped with safety valves (of both the check and pop-off types) of capacity sufficient not only to allow escape of vapors due to normal pressure increases, such as atmospheric temperature changes and movement of liquid into or out of the tank but also to allow the escape of abnormal amounts

of vapor that might result from heating of the tank by an outside fire. An excess flow valve which automatically closes also is recommended for above ground tanks so that their contents will not be dumped on the ground by a line break or similar accident. Buried tanks should be coated with bitumastic or plastic paint to protect against corrosion while above ground tanks require the protection of a heat reflecting coating, such as aluminum or white paint.

RECORDS (34) of fire insurance companies indicate on the one hand that 10 to 20% of fires are extinguished before fire companies arrive and on the other hand that 50 to 90% of all fires could be extinguished before fire companies arrive, if proper fire fighting equipment at the plant is provided and prompt action taken. It has been said many times that the best way to fight a fire is to prevent it from starting. However, since fires probably always will be with us, adequate fire fighting equipment should be provided and a fire fighting plan mapped out as part of the laboratory or plant safety program. An automatic sprinkler or carbon dioxide system may be suitable in some instances but, since streams of water frequently are not effective against solvent fires, a sprinkler system should be supplemented by other means of quenching fire. An ample supply of portable extinguishers of the carbon dioxide or foam type should be available at various points throughout the laboratory or plant, the carbon dioxide type being especially good for fighting fires around motors or other electrical equipment. Water fog delivered from special atomizing nozzles is especially good for smothering fires of practically all types, even those involving open tanks of solvent or solvent mixtures, such as a vat of paint; this is true likewise of the mechanical foam, which can be generated in large volume rather easily from simple equipment. Both "water fog" and "mechanical foam" have a cooling effect as well as an air-excluding or smothering effect on a fire, two fundamentally desirable features.

Workmen, of course, should be taught how to handle whatever fire fighting equipment is available. Also, it is worthwhile to consult with the city fire department people beforehand so that the plant fire fighting equipment and methods mesh with theirs insofar as practicable. Thus confusion is avoided and time saved upon arrival of fire companies if a serious fire should occur. Automatic fire doors at many plants are a worthwhile addition to fire fighting efforts.   •

Tankcars and trucks should be grounded both before and during the unloading operation if a combustible solvent is involved. Finally, it might be said that, as a matter of good chemical control, incoming shipments of solvent should be tested sufficiently to establish whether or not the material is that ordered or regularly in use since there always is the possibility that the wrong or off-quality material may have been shipped. Thus, a routine quick test on incoming shipments before unloading may more than pay for itself some day by preventing contamination of the solvent stock.

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