in acid. The effect on the slope of the tie lines of the increase from 25–35°C is small in all of these furfural–water–acid systems.

Othmer and Tobias (*5*) have shown that binodal curve data may be conveniently correlated through the equation

$$\log\left(\frac{100 - b_2}{b_2}\right) = m \log\left(\frac{100 - a_1}{a_1}\right) + n$$

where for the present system, a_1 is the mol % furfural in the furfural-rich phase and b_2 is the mol % water in the water-rich phase. The plots for the present system are linear, and the constants by least-squares treatment of the data at 25° and 35°C, respectively, are: $m = 0.8375$, $n = -1.0183$; $m = 0.9412$, $n = -1.0682$. The plait points have been obtained with the aid of these plots (*4*), and the results are included in Table I and Figure 1. Also included in Figure 1 for comparison are the plait points for the acetic, propionic, and butyric acid systems (*3*, *4*). The plait points in the formic acid system occur at a furfural-to-water ratio greater than unity. This ratio is less than unity for the plait points in the other three acid systems. In each acid system, the furfural-to-water ratio at the plait point increases as the temperature is increased.

The effectiveness of extraction of a solute by a solvent is given by the selectivity (*10*), which in the present work is a measure of the ability of furfural to separate water and acid.

Selectivity may be defined here as x/y, where x is the ratio of solute (acid) wt % concentration in the furfural-rich phase to that in the water-rich phase, and y is the ratio of water wt % concentration in the furfural-rich to that in the water-rich phase. The selectivities of the formic acid system at 25° and 35°C, and of the other acid systems at 25°C are given in Figure 2. The selectivity is lowest in the formic acid system, and this system exhibits maximum selectivity at about 3 wt % acid in the furfural-rich phase.

LITERATURE CITED

(1) Akopov, E. K., Voitko, L. M., *Izv. Vyssh. Ucheb. Zaved., Pishch. Tekhnol.*, 1966 (6), p 34.
(2) Dunlop, A. P., Stout, P. R., Swadesh, S., *Ind. Eng. Chem.*, **38**, 707 (1946).
(3) Heric, E. L., Blackwell, B. H., Gaissert, L. J., III, Grant, S. R., Pierce, J. W., *J. Chem. Eng. Data*, **11**, 38 (1966).
(4) Heric, E. L., Rutledge, R. M., *ibid.*, **5**, 272 (1960).
(5) Othmer, D. F., Tobias, P. E., *Ind. Eng. Chem.*, **34**, 693 (1942).
(6) Petunina, N. I., Chufarova, I. G., *Tr. Inst. Khim., Akad. Nauk SSSR, Ural. Filial*, 1968 (18), p 33; *CA*, **73:** 49072w (1970).
(7) Quaker Oats Co., Chicago, Ill., *Bull. 203-B*, p 4 (1968).
(8) Skrzec, A. E., Murphy, N. F., *Ind. Eng. Chem.*, **46**, 2245 (1954).
(9) Spaccamela Marchetti, E., Cereti Mazza, M. T., *Ann. Chim. (Rome)*, **59**, 902 (1969).
(10) Treybal, R. E., "Liquid Extraction," 2nd ed., p 43, McGraw-Hill, New York, N.Y., 1963.

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Flammability Characteristics of Methylene Chloride (Dichloromethane)

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Studies have been made to determine the effects of temperature, pressure, and additives on the flammability of methylene chloride vapors in air. Flammability diagrams for methylene chloride and for methyl alcohol in oxygen-nitrogen atmospheres are presented, together with diagrams showing the effect of methyl alcohol and of tertiary butyl alcohol on the flammability diagram of methylene chloride in air. It was determined that methylene chloride becomes flammable at 80°F and 760 mm Hg at a vapor concentration of 17% (by volume) with the addition of less than 0.5% (by volume) of methyl alcohol. Pure methylene chloride vapors in air become flammable at approximately 217°F at 760 mm Hg and at 80°F at 1280 mm Hg absolute.

Dichloromethane, methylene chloride in more popular terminology, is a common solvent often considered to be nonflammable. Because of extensive use in large quantities by many companies, a thorough study of those conditions which contribute to flammability was in order.

An explosive limits apparatus was employed, adapted so that limits could be determined at a wide variety of pressures and temperatures. The primary aims were to determine upper and lower flammable limits at atmospheric pressure and the effects of pressure and temperature on those limits.

Changes in the flammable limits because of admixture with known flammable solvents were also to be explored since methylene chloride is commonly used in mixed solvent systems.

PROCEDURE

Flammability results were based on visual observations of upward and outward flame propagation from a 12-kV arc-ignition source centrally located in a 5-liter spherical flask (Figure 1). The flask was contained in a small oven equipped with a heavy duty hair-dryer type of heater which permitted variation and control of apparatus temperature. *Caution:* Tests should commence at concentrations known to be outside the flammable range, with limits being approached in small increments. Violent explosions are possible with stoichiometric and near-lower-limit mixtures, with tests run at elevated pressures, and with tests run in strong oxidizers. Thus, all testing of this nature in simple glass equipment should include the use

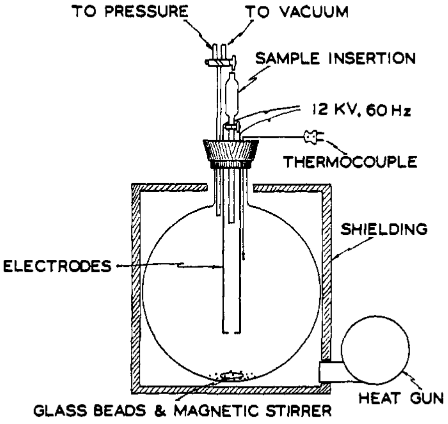


Figure 1. Five-liter explosive limits apparatus

of adequate shielding to protect personnel and the surrounding equipment in the event of vessel rupture.

In this investigation the flask and its thermostated container were placed in a well-shielded totally enclosed laboratory hood. The hood was equipped with electrical interlocks which prevented operation of the ignition arc with the hood door open.

To determine flammable limits, the flask was cleaned and evacuated prior to insertion of the liquid sample. The sample was measured with a microliter syringe and introduced through the sample insertion funnel. After being allowed to vaporize, it was mixed with air for time periods varying from $1\frac{1}{2}$–4 min, depending on the temperature at which the test was made. Air addition, up to atmospheric pressure, was made through the sample insertion funnel to ensure complete sample entry. At pressures above atmospheric, additional clean dry compressed air was added prior to mixing. Four to 12 separate tests were necessary to determine each limit value.

Vapor concentrations at the various temperatures and pressures were calculated on the basis of system and liquid sample volumes, assuming ideal gas law behavior.

Lower limit values, with the exception of those for mixtures with high percentages of methylene chloride, are reproducible within $\pm 2\frac{1}{2}\%$ of the value given. This reproducibility is primarily limited by the precision of liquid sample measurement, since there is a sharp break between flame propagation and lack thereof in the lower limit region. Upper limits and limits for the less energetic methylene chloride mixtures may be somewhat more in error, being perhaps $\pm 5\%$ of the value given since flame propagation is very slow just within the flammable region. More precise values could be obtained in a long tube apparatus, of adequate diameter, where flammability is based on flame propagation for a considerable distance from the ignition source, and not to great extent on operator judgment.

RESULTS

Pure Vapors. *Temperature.* Methylene chloride differs from conventional solvents in that at atmospheric pressure and room temperature it is not flammable. To illustrate conventional flammability, the diagram for methyl alcohol, based on data obtained on this apparatus by this laboratory, is shown in Figure 2. The location of the intersections of the vapor pressure and the explosive limit curves agrees well with the data (*8*). For methyl alcohol, flammable mixtures fall into one of three regions: (1) mists, the section to the left of the vapor pressure curve, consisting of droplets suspended in a vapor-air mixture; (2) saturated mixtures, along the vapor-pressure curve; and (3) the most common region, unsaturated vapor-air mixtures, lying to the right of this curve. This diagram was determined at atmospheric pressure (760 mm Hg). Points *A* and *B* represent the temperature limits of flammability. These were obtained in this apparatus by operating with a pool of excess liquid in the flask. They do not lie on the extrapolated flammable limit lines because of slight vapor-phase association at conditions of saturation and the use of the ideal gas laws for calculating vapor concentrations.

Comparing the flammability diagram for methylene chloride (Figure 3) with Figure 2, we see that at atmospheric pressure the only flammable mixtures are unsaturated vapor–air mixtures, and that the lower temperature limit of methylene chloride is about 217°F. The Bureau of Mines reports a narrow flammable range for methylene chloride in air at 212°F for upward propagation in 10-cm diameter tubes (*4*). The apparent difference in temperature limits of flammability may be due to such items as minor impurities, differences in system geometry, and experimental error or a combination of these factors (see Mixtures).

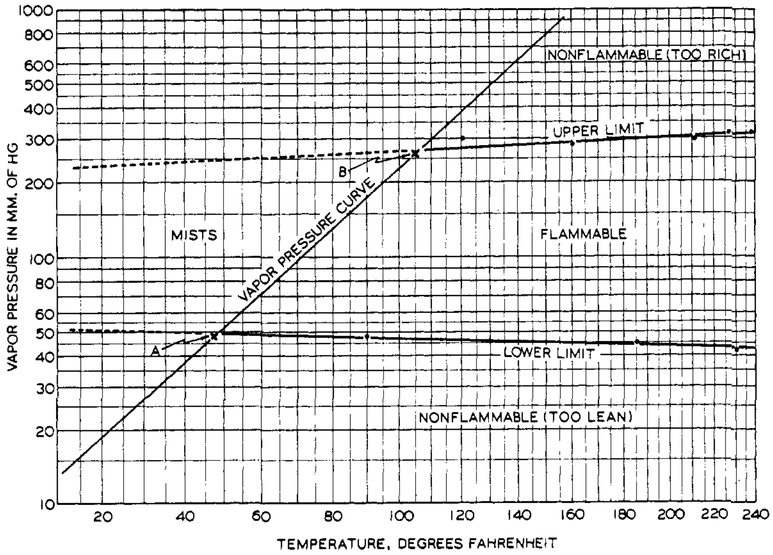


Figure 2. Flammability diagram: methyl alcohol in air

Total pressure: 760 mm Hg

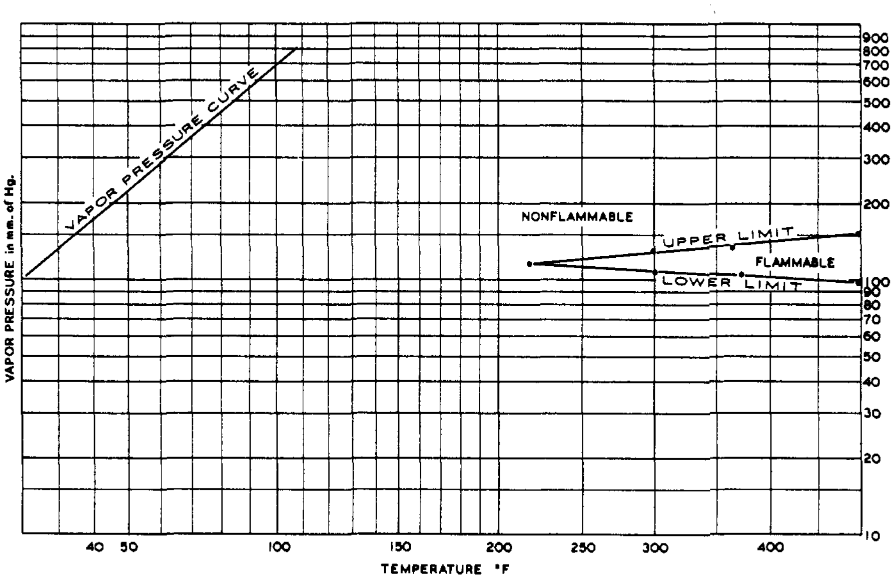


Figure 3. Flammability diagram: methylene chloride in air

Total pressure: 760 mm Hg

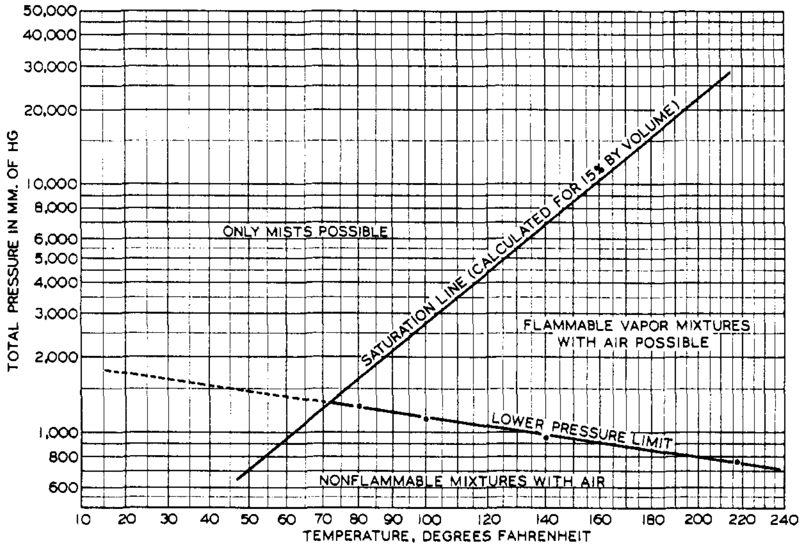


Figure 4. Pressure limits of flammability for methylene chloride in air

Pressure. The flammability diagram is useful for evaluating processes operating at atmospheric pressure, but many applications of methylene chloride call for the vapor to be subjected to higher pressures. Lower pressure limits of methylene chloride vapor were therefore determined as a function of temperature. Figure 4 illustrates the effect of temperature on the lower pressure limit and indicates that methylene chloride is flammable at room temperature (80°F) at a pressure of approximately 1280 mm Hg.

Figure 5 illustrates a useful concept in the presentation of flammability data (*8*). All of the relevant parameters of flammability (Table I) for pure methylene chloride are presented as a three-dimensional diagram with axes of pressure, temperature, and composition. With this system, it is possible to locate any process condition as a point on the diagram and thus determine how much of a safety factor exists in all directions.

The diagram, if extended, would exhibit a "top" constrained by vapor pressure limitations and a "bottom" which would show a diminishing range of concentration at temperatures above 217°F and pressures below atmospheric.

Inerting. One common method of dealing with situations in which flammable concentrations of combustible vapors are possible is to isolate those vapors in an inert atmosphere. The general effect of adding inert diluents to a vapor system is to narrow the flammable range for that system; that is, to raise the lower flammable limit and lower the upper flammable limit.

Figure 6 consists of two flammability diagrams showing the effect of the addition of carbon dioxide and of nitrogen on the flammable limits of methyl alcohol. For the carbon dioxide atmosphere, the upper and lower flammable limits converge until, at a carbon dioxide concentration of more than 33%, no methyl alcohol concentration is flammable.

Figure 7 shows the analogous effect of the addition of nitrogen to atmospheres of methylene chloride vapor. Figure 7 also indicates the effect of temperature on the inerting operation.

Vapor Mixture Systems. In many processes, methylene chloride is used in conjunction with other flammable solvents. For such situations, it is necessary to redetermine flammable limits for the mixture of vapors.

Figure 8 is the flammability diagram for mixtures of methyl alcohol and methylene chloride. Methylene chloride, although nonflammable by itself at room temperature and atmospheric pressure, acts as a flammable diluent, for it lowers the lower flammable limit of the methyl alcohol. Figure 9 illustrates the same relationships for *t*-butyl alcohol and methy-

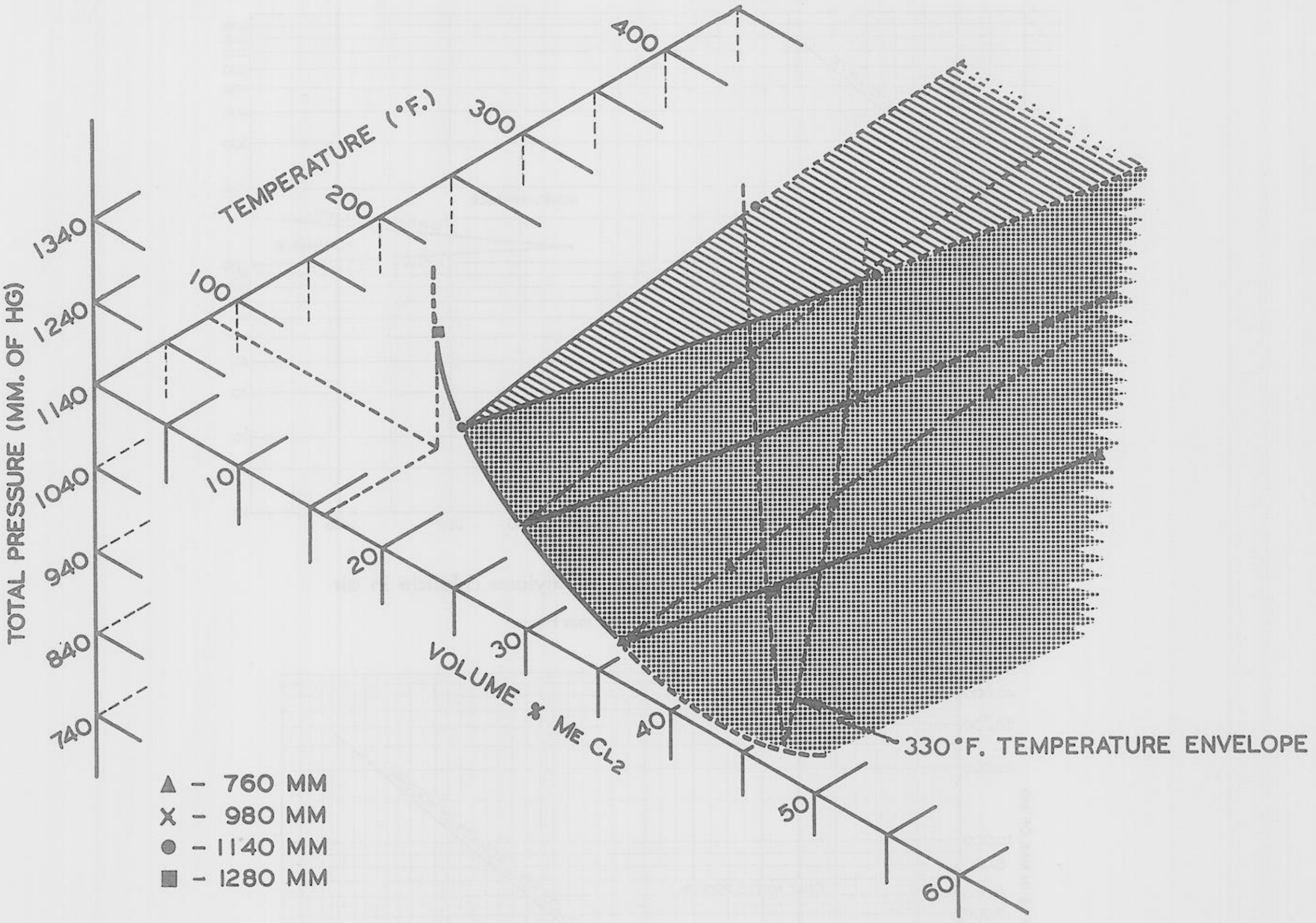


Figure 5. Flammability diagram for methylene chloride in air

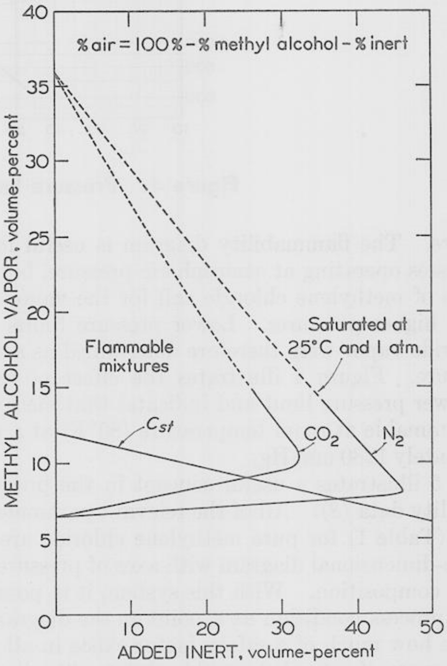
Table I. Effect of Temperature and Pressure on the Flammable Limits of Methylene Chloride in Air

Pressure, mm Hg	Temp, °F	Flammable limits, Vol % LEL	UEL
760	217	15.1	15.1
760	298	14.3	17.3
760	372	14.1	...
760	363	...	17.7
760	496	13.1	20.6
980	140	(15.3)	(15.3)
980	326	13.3	...
980	338	...	19.6
1140	100	15.4	15.4
1140	336	12.7	21
1280	80	16.0	16.0

lene chloride. Similar results for acetone–methylene chloride systems were reported by Coleman (*1*).

Points of special interest for these mixture diagrams include the "toe" point at various temperatures to indicate concentrations of methylene chloride above which no mixtures are flammable, as well as the lowest point on the curve for various temperatures, which indicates the minimum concentration of alcohol necessary to render methylene chloride flammable. With methyl alcohol, at 100°F and atmospheric pressure, no mixture is flammable at concentrations of methylene chloride greater than 26.5% (by volume). However, it takes less than 0.5% (by volume) of methyl alcohol to make a 17% (by volume) methylene chloride vapor flammable.

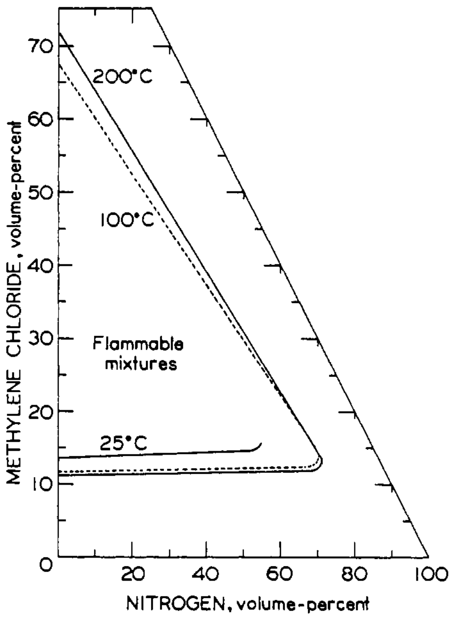
Flame caps (flames near the ignition source that do not prop-



Courtesy U. S. Bureau of Mines, Ref. 8

Figure 6. Limits of flammability of methyl alcohol–carbon dioxide–air and methyl alcohol–nitrogen–air mixtures at 25°C and atmospheric pressure

Broken curve at 50°C and atmospheric pressure



Courtesy U. S. Bureau of Mines, Ref. 4

Figure 7. Limits of flammability of methylene chloride–oxygen–nitrogen mixtures

1-Atm pressure; 25°, 100°, and 200°C

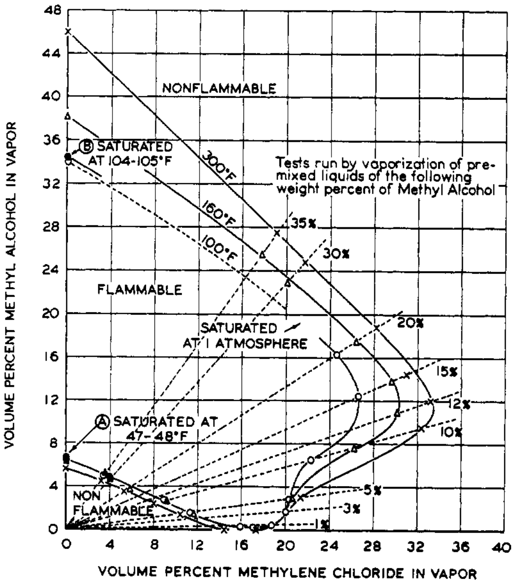


Figure 8. Limits of flammability of methyl alcohol–methylene chloride–air mixtures

(% Air = 100–% MeOH–% $MeCl_2$) 760 mm Hg

agate), when present with tests immediately outside of the flammable range, are indications that sufficient energy is available for ignition (*8*). These flame caps were noticed at all concentrations immediately outside of the limit values illustrated on the flammability diagrams.

Other sources (*4*, *5*) indicate that the vessel size used in these tests is sufficient to eliminate any significant effect of quenching of the flame by the walls of the vessel. It is felt that the results obtained in these tests are valid for application to processes in which similar conditions prevail.

It should be stressed that these data are presented in terms of vapor composition. (For ease of manipulation, the data were obtained by total vaporization of premixed liquids.) It is estimated, on the basis of available vapor-liquid equilibrium data (*7*), that *under equilibrium conditions* a methylene chloride–methyl alcohol liquid mixture containing as little as 0.2 wt % alcohol would evolve vapors containing 0.5 vol % alcohol. (There is little data in ref *7* in this concentration range.) Variables such as total pressure, degree of super heating, vapor densities of the two components, and degree of air movement would of course have a significant effect on the composition of vapor mixtures found in practice.

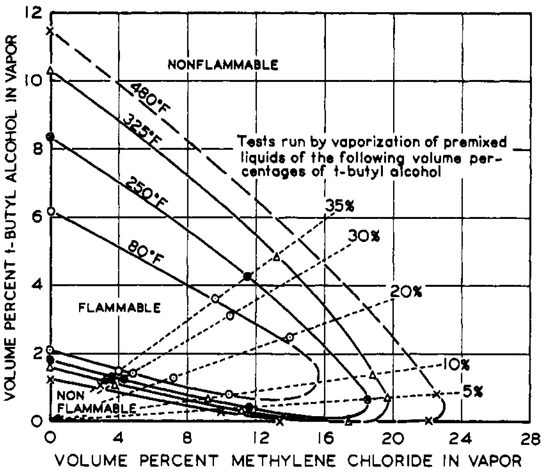


Figure 9. Limits of flammability of *t*-butyl alcohol–methylene chloride–air mixtures

(% Air = 100–% *t*-butyl–% $MeCl_2$) 760 mm Hg

DISCUSSION

The situation concerning methylene chloride's "nonflammability" might be compared to that of a few years ago for trichloroethylene. This material was considered nonflammable at normal room temperature and atmospheric pressure (*2*), and is so listed in certain of the literature to date. However, in 1963 (*6*), the flammability characteristics of trichloroethylene were finally determined and published. These were revised in 1966 (*5*).

A report (*3*) discussing a methyl bromide air explosion (this material was long considered practically nonflammable) states that any vapor normally considered nonflammable should be suspect if an exothermic combustion reaction with oxygen can be written. This is possible for methylene chloride.

CONCLUSIONS

Data included in this report indicate that methylene chloride vapors are nonflammable in air at normal ambient conditions. However, slight traces of other solvents, elevated temperatures, or higher pressure conditions can render it flammable. For these reasons, it is recommended that processes involving methylene chloride should be carefully evaluated to ensure the presence of adequate safety factors to prevent potential fires or explosions with this "nonflammable" solvent.

LITERATURE CITED

(1) Coleman, E. H., *Ind. Chem.*, p 211, May 1960.
(2) Coward, H. F., Jones, G. W., U.S. Bur. Mines, *Bull.* 503 (1952).
(3) Hill, H. W., *Chem. Eng. Progr.*, **58**, 46–9 (1962).
(4) Kuchta, J. M., et al., *J. Chem. Eng. Data*, **13**, 421–8 (1968).
(5) Perlee, H. E., et al., U.S. Bur. Mines, R.I. 6766 (1966).
(6) Scott, G. S., *ibid.*, 6190 (1963).
(7) Tenn, F. G., and Missen, R. W., *Can. J. Chem. Eng.*, **41**, 12 (1963).
(8) Zabetakis, M. G., U.S. Bur. Mines, *Bull.* 627 (1965).

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