The Dangers of Explosion* With Inflammable Liquids and Vapors By W. Payman

THE danger of explosion due to the ignition of mixtures of inflammable vapors and air is present in many common industrial occupations. It is important that the extent of this danger should be realised so that necessary precautions may be taken when handling or using liquids, such, for example, as benzol and gasoline, which yield inflammable vapors. The exact determination of the factors which decide the liability of a given liquid to give explosive mixtures presents a number of experimental difficulties and perhaps for this reason, has not attracted many investigators; but some information of value to technical chemists may be found scattered in chemical literature.

The nature of the danger to be apprehended during the use of inflammable liquids will depend upon the process or processes being employed. These may be divided roughly into three classes:

(1) Processes in which the liquids are used for crystallisation, precipitation, or as solvent media, or where they are being chemically treated as in sulphonation and nitration.

(2) Processes carried out in drying stoves or rooms, heated externally or by hot air blast, in order to remove the liquids from finished chemical products, with or without the subsequent recovery of the vapors by condensation or washing.

(3) Storage of liquids in tanks, and their transfer therefrom to plant or containers.

Throughout all such operations the danger arising from accidental leakage must also be taken into account.

The two most important criteria for judging the liability of a given liquid to produce dangerous conditions are:

(1) The volatility of the liquid.

(2) The range of explosion of the vapor when mixed with air.

Each inflammable vapor has a definite range of explosibility when mixed with air. Mixtures containing less than a certain percentage of vapor, known as the lower limit of inflammability, will not allow the continued propagation of flame, though a source of heat of sufficient intensity may cause a local ignition. If the percentage of vapor be increased, a point, called the upper limit of inflammability, is at last reached when the mixture is again incapable of propagating flame, and no mixture containing a greater percentage of vapor than this upper limit mixture will give more than a local inflammation.

The limits observed experimentally differ slightly with different positions of the point of ignition, as the flame may be helped or retarded by convection currents according to whether it has to pass upwards or downwards. For a detailed consideration of the experimental determination of the limits of inflammability of gas mixtures reference should be made to the work of Coward and Brinsley (Trans. Chem. Soc., 1914, 105, 1859; J.S.C.I., 1914, 33, 851), and Burgess and Wheeler (Trans. Chem. Soc., 1914, 105, 2591; J.S.C.I., 1914, 33, 1194).

It will be understood that, other things being equal, a vapor which gives with air mixtures having wide limits of inflammability will be more dangerous than one having narrow limits. For example, acetone, with a range of 6.15 per cent. (i. e., between 2.35 per cent. lower and 8.50 per cent. upper limit of inflammability), is more dangerous than benzol, with a range of only 3.3 per cent. (1.4 to 4.7 per cent.). The appended table gives the limits of inflammability of the commoner organic solvents as recorded by different observers.

The vapor pressure of the liquid may be so small at the temperature at which it is used as to be incapable of forming a lower limit mixture with the surrounding air. On the other hand a highly volatile liquid may easily give mixtures which are above the upper limit of inflammability. In the latter event it is important to note that the full range of inflammable mixtures has to be passed through before the percentage of vapor in the air renders the mixture safe; and, when this "safe" mixture has been attained, if the chamber be opened at any time to the outer atmosphere an explosive mixture would soon be formed by the inward diffusion of additional air.

From a knowledge of the vapor pressures of an inflammable liquid at different temperatures, coupled with a knowledge of its "limits," we can predict the working temperature at which the vapor pressure is (1) just sufficient to give a lower limit mixture, and (2) just sufficient to give a higher limit mixture. What may be termed the lower limit temperature of a volatile liquid corresponds in a sense to the "flash point" of an oil, though the latter, as determined by

the recognised methods, has no absolute meaning, the results being only relative. It must be remembered, however, that still air does not become saturated with a vapor for a considerable time, and so both the calculated limit temperatures may be lower than those actually required in practice to obtain the limiting compositions. Again, an increase in temperature widens the limits of inflammability, but from analogy with experiments with methane-air mixtures (Mason and Wheeler, Trans. Chem. Soc., 1918, 113, 45; J.S.C.I., 1918, 37, 115 A) it is unlikely that this effect will be appreciable over the range of normal working temperatures.

Two other factors are of importance when considering the inflammability of vapors:

(3) The speed of propagation of the flame in the mixtures with air.

(4) The ease of ignition of the mixtures.

The speed of propagation of flame is important whenever explosive mixtures are liable to be produced in long mains, as, for example, with acetone-air mixtures during the stoving of cordite (Wheeler and Whitaker, Trans. Chem. Soc., 1917, 111, 267; J.S.C.I., 1917, 36, 587). It should be noted that the speed of the flame in mixtures of a given vapor with air varies with the vapor content, being at a maximum when the percentage of vapor lies about midway between the limits, and falling rapidly as the limiting compositions are reached.

When considering the prevention of explosions, careful attention must be paid to the possibility of ignition of vapor-air mixtures by mechanical means, due to faulty or normal working of machinery in contact with the vapors. Sparks caused by grinding of ill-fitting parts, or the overheating of bearings due perhaps to similar causes, may be mentioned as possible sources of ignition. Unfortunately very little information is available on this point. Its importance has long been realised by mining engineers, but they have only examined the special tools and machinery used in coal mining to see whether sparks caused in operation would be powerful enough to ignite mixtures of fire-damp and air. (Compare, for example, Meyer, Oesterr. Z. f. Berg- u. Hüttenwesen, 1886, 34, 379.)

The prevention of explosions during storage and transference of inflammable liquids has perhaps received most attention. It will be readily understood that the use of compressed air for moving inflammable liquids from vessel to vessel is attended with great danger. In its place compressed flue gas, nitrogen, carbon dioxide or other "inert" gas may be used with advantage, as the risk of explosion is no longer present if there be insufficient oxygen in the atmosphere in contact with the liquid. In this connexion reference may be made to some work by Burgess and Wheeler (Trans. Chem. Soc., 1914, 105, 2598; J.S.C.I., 1914, 33, 1194), which showed that if the oxygen content of the air was reduced below 13.25 per cent. no mixture of methane with such an atmosphere was capable of propagating flame. The same point, and also the effect of added carbon dioxide, has been studied by Clement (U.S.A. Bureau of Mines, Tech. Paper 43, 1913; J.S.C.I., 1913, 32, 1149). This use of inert gas was first suggested by Bunte, and finds application in the patents of Martini and Hüneke (Ger. Pats. 146161, 149086, 150712 and 153703; see J.S.C.I., 1910, 29, 547) and others dealing with the safe transfer and storage of inflammable liquids. The addition of carbon tetrachloride, used largely in fire extinguishers, has been suggested by many authors as a means of rendering liquids non-inflammable, but according to Pfister (Z. angew. Chem., 1905, 21, 1786) the quantity required to be thoroughly effective is far greater than the volume of liquid treated.

Methods of extinguishing burning liquids are discussed by Burrell (U. S. A. Bureau of Mines, Tech. Paper 127, 1915), who also describes the precautions necessary in handling inflammable liquids.

TABLE.

Substance	Lower limit	Corresponding temp.	Upper limit	Corresponding temp.
Benzene	1.4	5	4.7	5
Toluene	1.4	7	4.7	30
Ethyl Alcohol	4.0	15	13.6*	35
Methyl Alcohol	7.8	13	18.0	26
Ethyl Ether	1.8	{ Below -30	5.2	-28
Acetone	2.35†	{ Below 20	8.5†	{ Below 20
Carbon Disulphide	4.1	{ Below 20	—	—
Petroleum Benzine	1.1	—	3.8	—
Gasoline	1.5†	—	5.3†	—
Pentane	1.35‡	Below 0	4.50‡	Below 0

In general, the precautions to be taken to prevent explosions will depend upon the individual process, but enough will have been said to indicate the factors to be considered in devising suitable methods.

The limits of inflammability are expressed in percentages by volume, and refer to the downward propagation of flame. Unless otherwise stated the determinations are by Kubierschky (Z. angew. Chem., 1901, 14, 129; J.S.C.I., 1901, 20, 345).

The "Limit Temperatures" have been calculated from the vapor pressures recorded in Landolt and Bornstein's Physikalisch-Chemische Tabellen, 1912

The Anthocyanin Pigments in Plants

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studied very recently, thanks to new data regarding the mitochondria and the plastids.

There is a tendency today to believe that the great majority of the products elaborated by the plant cell, particularly chlorophyll, starch, the pigments, the "metachromatic corpuscles," are due to the activity of special "organites," the "mitochondria," which are comparable at all points to the organites of the same name which have long been known in the animal cell. These are true "electosomes" whose function it is to select certain materials proceeding from the activity of the cytoplasm. These mitochondria can be nothing other than the figuring of the differentiation of the plastids studied by W. Schimper. Contemporary cytologists, among whom Guillaumond deserves special mention, have had the good fortune to recognize a stage anterior to the plastid, and have thus made a great step forward in the knowledge of cellular differentiation. Researches of this sort are peculiarly attractive and safe because of the fact that the observation of preparations, fixed and colored according to special methods, is supported by the examination "upon the living" which are usually very easy to make.

If we observe young flowers we are able to perceive the presence in certain anthocyanin cells, of granules or "rods" the ensemble of which constitutes the chondriome of the cell. They become impregnated "with a phenolic compound" which will become anthocyanin (soluble pigment), and then these elements will dissolve in the vacuoles, whence, in this manner, the anthocyanin will emigrate.

Let us carry this study a bit farther along the lines laid down by Guillaumond and F. Moreau. Two cases present themselves: either the anthocyanin will be formed at the expense of a colorless phenolic compound produced within the mitochondria and dissolved in the vacuoles, or else it will appear immediately in the mitochondria.

This conclusion agrees with that arrived at by R. Combes who found, by a method purely chemical, that the anthocyanin is either formed in small particles in the cell or else results from the transformation of colorless phenolic products.

The colorless phenolic compounds present the same micro-chemical reactions as do the anthocyanin pigments: they turn iron salts black, reduce osmic acid, fix methylene blue, and are colored yellow by bichromate of potash. They are distinguished however by the fact that Courtonne's reagent (neutral solution of lead acetate) colors them yellow, while it colors anthocyanin green. To sum the matter up, it results from the investigations of Guillaumond (1913-15), and F. Moreau (1914), that there are produced in the mitochondria phenolic compounds which may either appear immediately in the state of anthocyanic pigments, or which may be born in the form of colorless products and acquire color later (this colored product sometimes even becomes colorless once more); in some cases indeed this colorless product always remains colorless. Under the name of anthocyanic products, therefore, it is proper to include not only the red, blue or violet pigments already known under that term, but also the colorless compounds whose study is inseparable from that of the former. Mirandi, in 1916, also confirmed the Mitochondrial origin of the anthocyanin of a Pteridophyte.

In works appearing anterior to these researches it was the custom to contrast the anthocyanins with the other pigment under the name of "soluble pigments"—chlorophyll and xanthophyll being always fixed in the plastids. The "soluble pigments" are dissolved in the cell sap. But as we have just seen the anthocyan also exhibits a mitochondrial or plastidary origin, and the state of solution in the cell sap of the vacuoles represents merely the final stage in the evolution of the pigment.

To complete the history of the evolution of anthocyanin in the cell it should be pointed out that its concentration in the cell sap may become so great that the pigment will separate out in either an amorphous or a crystalline form; this separation is easily obtained *in vitro*. In 1906 Gertz compiled a long list of examples from various sources, especially Courchet, Molisch, etc. Finally, when the tissues die or become lignified, it may occur that the anthocyanin will be observed by the cellular wall and color it.

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