THE STORAGE AND TRANSMISSION OF HAZARDOUS LIQUIDS

By S. F. GROVER, B.Sc.(Eng), A.M.I.Mech.E.* and B. G. WILSON, A.M.C.T., A.M.I.Mech.E.*

SUMMARY

The authors discuss in general terms the methods of combating some of the hazards involved in handling dangerous liquids.

Introduction

It is desirable at the outset to clarify the meaning of " hazardous liquids " in this context. The materials of which the authors have experience and which they regard as hazardous include molten lead, mercury, chlorine, bromine, sodium, caustic soda, sulphuric acid, hydrochloric acid, ethyl chloride, ethylene dibromide, ethylene dichloride, and tetra-ethyl lead. It is obvious that the hazards are not the same with all the fluids. Analysing the difference leads to the suggestion that four types of hazards exist, *i.e.*

1. Toxicity
2. Skin burns
3. Explosion and fire
4. Corrosion.

A fifth classification would be that of radiation, but this is excluded because the authors have no experience in this field.

The difference in overall hazard from one material to another arises from the fact that the relative importance of the individual hazards varies. For instance, molten lead can give off toxic fumes and can cause skin burns, but it is not likely to give rise to any explosion risks. Tetra-ethyl lead is highly toxic but not likely to cause skin burns.

If, having analysed the hazards arising from any given material into these categories, one could apply firm rules for combating each hazard the designer's task would be easy. However, generalising is dangerous and may either lead to inadequate safety or uneconomic design. Having warned of the dangers of generalisation, the authors offer the following suggestions for combating the various types of hazards.

The first is that unless it is absolutely essential, toxic materials should not be stored or pumped. If possible, it is better to feed the material directly into the next process and convert it into a less hazardous material. For instance, where bromine is produced for the formation of ethylene dibromide, the bromine should be fed directly into the ethylene dibromide plant with the minimum of buffer capacity. Another suggestion is that vapours of the toxic liquid should be kept out of the atmosphere. Tanks should be enclosed and any vents should be scrubbed or led to a point away from any personnel. To avoid vapour-laden air being emitted when tanks are being filled, the vents can be connected back to the vessel from which the tank is being filled. One method of keeping the vapour concentration down in the vapour space in a tank is to float a layer of non-toxic liquid on top of the toxic material if an immiscible non-volatile liquid can be found.

When designing tanks for liquefied gases some assistance may be obtained from D.S.I.R. Gas Cylinders and Containers Committee report, entitled *Revised Recommendations for Welded Containers for the Commercial Transport of Chlorine, Phosgene, Ammonia and Sulphur Dioxide in the Liquified State*.[1] Further information on filling ratios is given in B.S.1736 : 1951.[2] These recommendations relate to transport containers but the information can be used for static installations. No pressure relief devices are called for by these recommendations but, on static installations, it may be desirable to incorporate a safety vale. In order to prevent seepage through safety valves it is common practice to back-up the valve with a bursting disc.

Making absolutely sure that highly toxic materials are completely contained can be expensive and it may be economic to control the vapours after escape by ventilation. If this is done it is necessary to know the maximum allowable concentration (M.A.C.) in the air which a person may breathe safely for a limited period of time. M.A.C. values used for industrial purposes assume exposure of eight hours per day for a five-day week and are expressed in parts per million by volume for gases and milligrams per cubic metre for particulates. The latter is sometimes expressed in milligrams per 10 cubic metres, the volume of air breathed by a man in eight hours being approximately 10 cubic metres.

When designing ventilation systems it is good practice to employ tailored ventilation at all anticipated points of leakage such as pump glands, etc. The shape of hoods and air velocities required for adequate entrainment of escaping material will depend upon the form of emission and the characteristics of the material. Brandt[3] gives detailed recommendations for designers in this field. In enclosed buildings, any tailored ventilation system should be supported by general ventilation in order to prevent formation of stagnant air pockets where toxic materials may build up. It is desirable for the air extract system to have a capacity slightly larger than the heated air supply system so that a depression is maintained to prevent escape of contaminants to atmosphere.

In addition to keeping the vapour out of the atmosphere it is essential to keep the toxic liquid out of public sewers in the event of spillage. One method used towards this end is to surround the tank by means of a bund wall. Bunds should be constructed of or covered with non-absorbent material to ease decontamination. When designing bunds it is necessary to make arrangements by means of which the fluids can be

* The Associated Ethyl Company Ltd., Ellesmere Port, Cheshire.

reclaimed. This is often effected by a valved outlet to special chemical drainage system feeding back to a recovery plant or effluent treatment plant. If bunded tanks are installed outdoors, facilities must also be provided for removing storm water by providing a valved outlet to the normal storm water drains, usually via an interceptor. Bunds are, of course, designed to retain liquid after it is spilled. All precautions should be taken to see that spillage does not occur. To this end it is essential that the operator is provided with adequate and reliable means of knowing what is in the tank. A complete paper could be written on the subject of level indication but in this paper only one general comment will be made. Storage tanks for toxic materials should contain the minimum of equipment which will require maintenance. Any equipment which has to be removed for maintenance will add to the risk of air pollution.

Pumping toxic materials need not always be a problem. The use of glandless, canned-motor pumps or magnetic drives is frequently possible. In other cases vertical spindle pumps, arranged with extended spindle and casing so that these extend above the maximum liquid level in the feed tank, can be used. In this case a labyrinth gas seal is fitted above the liquid level and a distance piece between the seal and the combined thrust and journal bearing above the seal forms a chamber which is evacuated by connection to the ventilation extract ducting or a free vent suitably located. Transfer by vacuum or compressed air is often used, although this increases the problem of contaminated vents.

Piping can be conventional and the modern technique of all-welded lines has advantages in that it reduces the maintenance of joints. All lines must be self-draining to prevent liquid being trapped at low points because this can cause considerable air pollution if the lines are broken for maintenance. In some cases it may be desirable to install facilities for back washing the lines.

All these points of design should be backed up by a well-equipped safety organisation. The atmosphere should be monitored to ensure that concentrations above the M.A.C. are not reached. Air masks, protective clothing, and chemicals for decontamination should be readily available. Bathing facilities must be immediately to hand where toxic materials which can be absorbed through the skin are being handled.

Finally, care should be taken that the design meets the requirements of the Factories Act 1959[4] and the Alkali etc. Works Regulation Act 1906[5]. Also compliance with any Local Authority bye-laws and regulations must be ensured.

Skin Burns

Skin burns may be thermal or chemical. Thermal burns differ from the other hazards referred to in this paper in that they can occur when the hot liquids are completely enclosed in vessels and piping. However, adequate lagging can overcome this hazard and this precaution is seldom forgotten because of the need to conserve heat. Leakage of hot liquid can also be a problem and in this connection tanks and piping should not be installed over areas frequented by operators unless precautions are taken to retain spillages.

For chemical burns the liquid must contact the skin and in consequence leakage should be eliminated. Overhead installations should be avoided if possible. Joints in pipework should be kept to a minimum and an added safeguard is to wrap the gap between flanges and other potential points of leakage with suitable material to prevent any escaping fluid forming a jet which may hit passing personnel. Typical examples are the use of lead for wrapping joints in sulphuric

acid lines, mild steel strips for caustic soda lines and rubber backed by steel for hydrochloric acid lines. This precaution can also reduce the risk of accidents when joints are being broken for maintenance. Drain and sampling connections should be run to safe points for disposal and where the latter are concerned protection for the operator's face should be provided. Drains taken to gulleys should be arranged to enter the gulley and to discharge without splashing.

The precautions against skin burns are basically common sense and in consequence little is said on this subject. However, in 1958, out of a total of 5869 accidents in the chemical industry, 527 were due to injuries from molten metal and other hot or caustic substances.[6] There would appear to be a need for a more rigorous application of common sense.

Explosion and Fire Hazards

Explosion and fire hazards are grouped together because they both arise from the handling of flammable liquids. Many of the precautions to combat the explosion hazard are similar to those used against the toxic hazard and in consequence these will be dealt with first. The main differences between toxic hazards and explosive hazards arise from the fact that toxicity is a hazard to personnel only, whereas explosions can damage plant as well. Also explosions in confined spaces can do more damage than those in the open, and explosions can lead to fire.

As with toxic hazards, when there is a possibility of fire or explosion it is desirable to ensure that vapours are not allowed to escape in quantity. With toxic hazards the important criterion is the M.A.C. figure. With explosive hazards the criterion is the Lower Explosive Limit. Fortunately, Lower Explosive Limit concentrations are usually a few per cent expressed in volume ratios and not parts per million as for toxic hazards. Unfortunately, many flammable liquids are volatile and give explosive mixtures in equilibrium with the liquid at relatively low temperatures. The temperature at which explosive mixtures are in equilibrium with the liquid under specified conditions is known as the " flash point " of the material. Two common conditions specified lead to the terms " Closed Cup Flash Point " and " Open Cup Flash Point ", the latter being a higher temperature than the former. These properties will be referred to frequently in the next few paragraphs.

The fact that an explosion in a confined space causes more damage than one in the open leads to the recommendation that storage of flammable materials should be outdoors. The relatively high concentration associated with the Lower Explosive Limit reduces the degree of ventilation required to dilute escapes to safe limits compared with toxic materials. In consequence natural air movements can be used except in a few cases where leakage is likely to be heavy.

It must be remembered that, in tanks containing liquids above their closed cup flash point, the vapour space will contain an explosive mixture unless precautions are taken. Floating roof tanks or blanketing with an inert gas may be used to overcome this. Some people argue that explosions are not likely to take place in enclosed vessels because no source of ignition is present. Sources of ignition may arise from many apparently innocent conditions and static electricity has been shown to be capable of causing an explosion.[7] Mention should be made here of the use of flameproofed electrical equipment to B.S.229[8] and of intrinsically safe electrical equipment to B.S.1259.[9] In both cases, certificates that the equipment has passed the appropriate tests at Buxton and Sheffield respectively should be insisted upon. The difference

between the groups of B.S.229 and the classes of B.S.1259 is worth noting. There should be no need to mention that naked flames should be kept out of explosive hazard areas, but the fact that some aluminium paints on rusty steel surfaces can cause sparks under certain conditions is often overlooked. The difficulty of defining the types of aluminium paint which are safe under all conditions has led to the banning of all aluminium paints on steel surfaces by at least one company.

When designing storage installations for flammable liquids it is essential to review the properties of the liquid and to determine which of the government regulations are relevant. Certain materials with a closed cup flash point below 73°F are covered by the Petroleum (Consolidation) Act 1929[10] and by the Petroleum (Mixtures) Order 1929.[11] Typical materials are crude petroleum, gasoline, benzene, heptane, hexane, octane, naphtha, and toluene. Storage of these materials requires a licence and in order to obtain a licence the installation must conform to the requirements of the local authority which normally bases its regulations on the Petroleum-Spirit Model Code.[12] This code gives details of the distance of tanks from boundary fences and from buildings, and the spacing of tanks relative to each other. The precautions to be taken with regard to sources of ignition such as electrical apparatus, static electricity, carrying of matches, boiler houses, and locomotives are listed. Some regulation relating to the design of the tanks (such as minimum plate thickness for above-ground and underground tanks) together with the requirements for tank fittings are given. Figures given in the Act are not quoted in this paper because it is felt to be dangerous to extract them from their context. If difficulty is experienced in obtaining copies of the Model Code similar information is available in Watts.[13]

Many flammable materials with flash points above 73°F are used in industry. Some guidance as to the precautions to be taken with these can be obtained from the Institute of Petroleum Safety Codes,[14] Parts I, II and III. In this code inflammable materials are grouped into

Class A—flash points below 73°F

Class B—flash points between 73°F and 150°F inclusive

Class C—flash points above 150°F.

Class A materials line up with those covered by the Petroleum (Consolidation) Act 1929 but further information is given in the code on the spacing of tanks and on the method of bunding tanks to prevent spread of fire.

Class B liquids are accepted as less hazardous than Class A liquids but, for refinery use, the recommendation is given that tanks for Class B liquids should be treated similarly to those for Class A in order to provide flexibility. Where Class C materials are concerned the fire risk is regarded as being quite small and no restrictions are placed upon the spacing of tanks and bunding is not recommended except where oil might escape and cause damage to a third party. Many people regard this last point, together with the recovery of large spillages, sufficient justification to include bund walls on installations for Class C materials.

The Institute of Petroleum Safety Codes are intended for application to refineries where the quantities handled are very large. In the chemical industry, where the quantities are often smaller, it is difficult to assess whether the recommendations of the I.P. Code should be applied or not. Here the I.C.I. Engineering Codes and Regulations,[15] available from the Royal Society for the Prevention of Accidents, may be useful. At the opposite end of the scale to the Institute of Petroleum Safety Codes is B.S.799 for oil-burning equipment.[16] This gives recommendations for the storage and piping of fuel oil with flash points above 150°F. B.S.2654 entitled *Vertical Mild Steel Storage Tanks, with Butt Welded Shells for the Petroleum Industry* is worthy of mention.[17]

Turning to some specific points not covered by these references; the specific gravity of the vapour can affect the precautions which should be taken. Where the vapour is heavier than air and has an asphixiant or anaesthetic property bund walls should be kept low to reduce the risk to operators. The use of pipe trenches and ducts are not recommended where heavier-than-air vapours are concerned, as these can cause the spread of explosive vapours and fire unless fire stops are incorporated. Above-ground piping makes the dispersion of vapours easier and thus reduces the risk of explosion. Lighter-than-air vapours are not common but where they do occur the use of large areas of solid staging should be avoided. This is especially so where the staging includes deep beams which can help to form pockets of explosive gas.

The need for flame traps on vents carrying flammable vapours is emphasised in many of the references quoted. In this paper only one specific point is made. When installing flame traps on tanks it is common practice to turn the end of the vent pipe over in a swan neck to prevent rain entering the vent. If this is done it is desirable to ensure that, should the vent be ignited, the flame produced does not impinge upon the tank, especially if the tank contains material with a low boiling point. The Texas oil fire gives a lesson on this point.[18] Tanks containing low-boiling-point liquids or liquefied gases should be fitted with water sprays to provide cooling in the event of a fire in the vicinity.

Static electricity has already been mentioned as a possible source of ignition. Most flammable materials are good insulators and in consequence are liable to generate static, especially if small concentrations of impurities are present. It is essential, therefore, to ensure that all equipment is satisfactorily earthed and all piping-flanges bonded for electrical continuity.

The specific comments given are somewhat haphazard but this has been caused by an attempt to refrain from quoting the various references at length.

Corrosion

The fact that a liquid is corrosive may not be regarded as being a hazard in itself. However, if it is combined with toxic, explosive, or other properties it may accentuate the hazard from that source. The first consideration should be to decide on the correct material of construction for the liquids to be handled, taking into account the economic life of the equipment. When dealing with hazardous liquids, safety in handling must not be forgotten but the introduction of this factor into economic equations is difficult. Generalised advice on this is impossible and only experience with a specific fluid and appropriate materials of construction can provide the answer. Laboratory tests on possible materials of construction may provide useful experience but care must be taken that all factors arising in the full scale design are taken into account during the tests. Variations in fluid composition, effects of impingement and velocity, galvanic action, etc., may all enter into the corrosive properties of a liquid. Plant trials are the only completely satisfactory answer but here, failure of equipment will introduce a plant hazard.

Having decided upon the material of construction, it is often necessary for the designer to incorporate a corrosion allowance over and above the design thickness for the equipment. This in itself is not sufficient unless inspection at

intervals is undertaken to ensure that the corrosion allowance has not been consumed. Inspection of vessels and equipment handling toxic materials can be expensive if it is not to introduce a hazard in itself. This should be taken into account when working out the economies of materials of construction.

Manhole covers on tanks requiring inspection should be larger than normal where toxic materials are concerned, to allow for passage of men wearing protective clothing. A suggested minimum is 20 in. diameter. Where the height of the manhole branch exceeds 24 in. the diameter of the manhole should be greater and a suggested minimum is 24 in. It should be emphasised that these minima are based purely on the grounds of safety. Other limitations are imposed by purely mechanical considerations, e.g. B.S.1500.[19]

General

When designing pipework to carry hazardous fluids of any sort it is essential to make it robust. Small bore piping should be avoided unless it is very well supported. Small bore connections on vessels should not be used unless adequately reinforced by stiffening ribs. A minimum size of 2 in. is recommended for such connections where practicable. Flanged piping is preferable to screwed fittings and welded pipe is even better in most cases.

Vessels to be installed out of doors which are unlagged should be constructed of steel with good impact strength at low temperatures. This is especially true if the vessel is subject to pressure. It is even more true if its contents have been chilled before entering the tank, but in this case it is less likely to be forgotten.

In the text, references have been given to a number of regulations and codes. Other references of a very general nature include the International Labour Office Model Code.[20] When considering this document care must be taken that local requirements imposed by statute or bye-laws are not more stringent. A second work of a general nature is the publication of the Association of British Chemical Manufacturers entitled *Safety Rules for Use in Chemical Works*,[21] and a third is the National Fire Codes.[22]

Conclusions

The design of storage, pumping and piping installations for handling hazardous liquids is a complex subject. In a paper of this length it is impossible to cover all points in detail but it is hoped that some of the general points raised may be helpful.

References

[1] " *Revised Recommendations for Welded Containers for the Commercial Transport of Chlorine, Phosgene, Ammonia, and Sulphur Dioxide in the Liquefied State (Document Ref 12C)* ". Published by the Gas Cylinders and Containers Committee of D.S.I.R. (London : H.M.S.O.) See also " Notes on Document 12C ", published by the Home Office 1955 (London : H.M.S.O.).

[2] " *Filling Ratios for Liquefied Gases* ", B.S.1736 : 1951 (London : The British Standards Institution).

[3] Brandt, A. D. " *Industrial Health Engineering* " (London : Chapman and Hall Ltd.).

[4] " *The Factories Acts* 1937, 1948, *and* 1959 " (London : H.M.S.O.).

[5] " *Alkali, etc. Works Regulation Act* 1906 " (London : H.M.S.O.).

[6] " *Chief Inspector of Factories Report for 1958* " (London : H.M.S.O.).

[7] Klinkenberg, A. and Van der Minne, J. L. " *Electrostatics in the Petroleum Industry* " (Amsterdam : Elsevier Publishing Co. Ltd.).

[8] " *Flameproof Enclosures of Electrical Apparatus* ", B.S.229 : 1957 (London : The British Standards Institution).

[9] " *Intrinsically Safe Electrical Apparatus and Circuits for use in Explosive Atmospheres* ", B.S.1259 : 1958 (London : The British Standards Institution).

[10] " *Petroleum (Consolidation) Act 1928* " (London : H.M.S.O.). See also " *Statutory Rules and Orders 1929 No. 952* " (London : H.M.S.O.).

[11] " *Petroleum (Mixtures) Order. Statutory Rules and Orders 1929 No. 993* " (London : H.M.S.O.).

[12] " *Petroleum (Consolidation) Act 1928. Model Code of Principles of Construction and Licensing Conditions Part II for Distributing Depots and Major Installations* " (London: H.M.S.O.). (Copies only available on written application by Local Authority.)

[13] Watts, H. E. " *Storage of Petroleum Spirit* " (London : Charles Griffen and Co. Ltd.).

[14] " *Institute of Petroleum Model Code of Safe Practice in the Petroleum Industry, Part I (Electrical Code), Part II (Marketing Safety Code), Part III (Refining Safety Code)* " (London : The Institute of Petroleum).

[15] " *I.C.I. Engineering Codes and Regulations : Group C—Electrical Engineering, Vol. 1.3 Plant Installation. Group D—Miscellaneous, Vol. 1.3 Fire Prevention* " (London : Royal Society for the Prevention of Accidents for Imperial Chemical Industries Ltd.).

[16] " *Oil Burning Equipment* ", B.S.799 : 1953 (London : The British Standards Institution).

[17] " *Vertical Mild Steel Welded Storage Tanks and Butt Welded Shells for the Petroleum Industry. Part I—Design and Fabrication* ", B.S.2654 Pt I; 1956. (London: H.M.S.O.)

[18] " *Texas Refinery Tragedy* ", in *Quart. nat. Fire Prot. Ass.*, Boston, October 1956.

[19] " *Fusion Welded Pressure Vessels for Use in the Chemical, Petroleum, and Allied Industries. Part I—Carbon and Low Alloy Steels* ", B.S.1500 Pt I : 1958 (London : The British Standards Institution).

[20] " *Model Code of Safety Regulations for Industrial Establishments for the Guidance of Governments and Industry* " (Geneva : The International Labour Office).

[21] " *Safety Rules for Use in Chemical Works. Part I—Model Rules. Part II—Detailed Information* " (London : The Association of British Chemical Manufacturers).

[22] " *National Fire Codes. Vol. I—Flammable Liquids, Gases, Chemicals, and Explosives* " (Boston, Mass : National Fire Prevention Association).

Appendices

Appendix 1 and Appendix 2 appear overleaf on p. 106.

Appendix 1

Toxic hazards

Of the materials listed in the paper, the following are regarded as toxic and the maximum allowable concentrations are given.

Lead	0·15 mg/m³
Mercury	0·10 mg/m³
Chlorine[a]	1·0 p.p.m.
Bromine[a]	0·5 p.p.m.
Ethyl chloride	1000 p.p.m.
Ethylene dichloride[b]	10 p.p.m.
Ethylene dibromide[b]	2 p.p.m.
Tetra-ethyl lead	0·075 mg/m³

[a] These are irritant gases and at concentrations slightly above the M.A.C. values become intolerably irritant subjectively.

[b] Toxic and anaesthetic. Contact with skin or eyes can cause superficial damage such as dermatitis and inflammation.

Appendix 2

Explosion hazards

Of the materials listed in the paper the following are regarded as flammable.

	Ethyl chloride	*Ethylene dichloride*
Vapour density relative to air	2·22	3·42
Vapour pressure at 20°C	1003 mm Hg	64·2 mm Hg
Boiling point.. ..	12·2°C (54°F)	83·5°C (182·3°F)
Lower explosion limit	3·8% v/v	5·7% v/v
Upper explosion limit	15·4% v/v	16% v/v
Closed cup flash point	−50°C (−58°F)	10°C (50°F)
Flameproof group (B.S.229) ..	II	II
Intrinsic safety class (B.S.1259)	Pentane	Pentane