SOME SIGNIFICANT CHEMICAL ACCIDENTS .

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SUMMARY

In deciding the precautions that should be taken to prevent accidents that may arise from causes of a chemical nature, certain simple principles are followed. Judgment must be exercised, however, in the apportioning of emphasis in the application of the principles. It is by the study and the investigation of accidents that one discovers the conditions that are most frequently associated with them and the conditions that give rise to the greatest disasters. This paper contains a description of some accidents that are typical of those that have led particular importance to be attached to certain precautions.

Introduction

For more than twenty years chemists in the Factory Inspectorate have followed a clearly formulated set of principles in determining the precautions that should be taken to prevent accidents that may arise from causes of a chemical nature. These principles are derived from the elementary, self-evident principle that, if a person is liable to suffer injury by contact with a dangerous substance, precautions should be taken to prevent the contact. In the present context contact may be direct or indirect. Injury from direct contact may occur, for example, when a man is splashed by corrosive material, in which case the contact is external, or when he breathes a poisonous gas or vapour, in which case the contact is internal. A dangerous substance may cause injury in another way when it burns or explodes. In this case the contact with the dangerous material is indirect.

The most effective way of ensuring that a person will not be injured by direct contact with a dangerous substance is to replace the dangerous substance by a safe one which is also capable of serving the purpose of the process. Alumina is used as a safe and effective substitute for silica in pottery saggars ; and steam or hot water (sometimes in conjunction with a wetting agent) can often be used instead of benzene for oil and fat extraction, thus avoiding the well-known danger associated with the inhalation of benzene vapour. Even when there is no completely safe material that can be used for the purpose served by the dangerous material, a considerable step towards safety is often taken by the substitution of a less dangerous one : trichlorethylene or white spirit are used nowadays for many purposes for which carbon tetrachloride or benzene were used in the past.

In many instances, however, a dangerous substance must still be used, and, in such a case, the principle that is followed in the prevention of contact is that of imposing a barrier between the dangerous substance and the persons who would otherwise be exposed to the danger. Fencing is provided round acid tanks, and lead shrouds are fitted round flanged joints in pipe-lines where leaks of corrosive liquids could take place. In processes from which poisonous gases, vapours, or dusts are liable to be evolved the barrier may take the form of complete enclosure of the plant with arrangements for operating the process from outside the enclosure. In such a case the enclosure may be under exhaust ventilation. A modern example of this type of enclosure is the glove-box so commonly used in the handling of radioactive materials. For the purposes of manipulation it is often necessary to provide an opening in the enclosing barrier. This opening should be no larger than is necessary for the operations that must be carried out, and the exhaust ventilation that is applied to the enclosure should ensure that the velocity of air passing through the opening from the workroom into the enclosure is such that there is no outward drift of toxic material into the air of the workroom. In other words the principle of the chemists' fume-cupboard in all shapes, forms, and sizes is followed. For purposes of maintenance it is often necessary that someone should enter a vessel that has contained a dangerous material. In such a case the vessel should be isolated and purged to remove gases and vapours with which the person entering would otherwise have contact. Sludge or scale should be washed out with a hose. After all this has been done the vessel should be tested for gas before entry. If sludge or scale cannot be removed before entry, the person entering should wear breathing apparatus and a life-line and a watcher should be stationed outside the vessel.

The principles governing the precautions to be taken in the case of substances that form flammable or explosive mixtures with air can be more briefly stated. When the process allows it, steps should be taken to avoid the presence of the flammable or explosive mixture. This may be done by the substitution of a non-flammable or a less flammable material, by the use of exhaust ventilation to remove flammable gases, vapours, or dusts, or by the use of inert gas. Sources of ignition should be eliminated as far as possible and precautions should be taken to minimise the spread and effects of a fire or explosion. In other words, a fire or explosion, commencing in a small way, should be prevented from becoming a large one, and an explosion, starting in some part of the plant where it would do comparatively little harm, should be prevented from spreading to a part where it could do injury and damage.

While the principles themselves can be described in a few minutes, the art of applying the principles is something that is learned over a life-time. It is by the study and the investigation of accidents that one discovers the conditions that are most frequently associated with them and the conditions that give rise to the greatest disasters. In this way a basis is established for the exercise of judgment in the apportioning of emphasis in the application of the principles. It has been proposed therefore that this paper should contain a description of some

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accidents that are typical of those that have led us to attach particular importance to certain precautions.

Gassing Accidents

Some of the worst gassing accidents have occurred to men who were working inside plant or other confined spaces. If a dangerous gas or vapour is liable to be present inside a confined space of this nature, the risk is obvious and stringent legal requirements indicate the precautions that aie deemed to be necessary when work has to be done in such conditions. It is not the purpose of this paper to consider in detail the requirements of the Factories Acts, but it should be noted in connection with what follows that Section 27 of the Factories Act, 1937 as amended by Section 6 of the Factories Act, 1959 requires that, where work has to be done inside any chamber, tank, vat, pit, pipe, flue, or similar confined space, in which dangerous fumes are liable to be present to such an extent as to involve risk of persons being overcome thereby, the confined space shall not be certified as safe for entry without breathing apparatus unless, amongst other precautions, effective steps have been taken to prevent any ingress of dangerous fumes. In Regulation 7 of the Chemical Works Regulations it is required that such a place shall be certified as isolated and sealed from any source of dangerous gas or fume. The lesson that was learned from the accident described in the following paragraph was that, if isolation in such circumstances is to be effective, it must be well designed to conform with high standards.

Examples and their lessons

In a chemical factory a battery of four pans was being used for a process in which hydrogen sulphide was generated. Each pan was connected by a short duct to a common main fitted with an exhaust fan to draw fumes away from the pans. On each duct was a valve for the purpose of shutting off the pan from the main. On the day of the accident three of the pans were working and were open to the main. The fourth pan was standing idle awaiting some minor alteration. It had been steamed out and washed clean the previous day, the valve had been closed with the intention of isolating the pan from the main, and all other pipes to the pan were disconnected. After mice had been exposed inside the pan for an hour for the purpose of testing the atmosphere and had shown no signs of distress a man entered to carry out the alteration in question, but he was called away a few minutes later to another job. He entered again an hour later, without further test, and was at once overcome and killed by hydrogen sulphide. Two men, who attempted a rescue without breathing apparatus, were also overcome and one of them died.

After the accident it was found that the belt had come off the pulley of the exhaust fan. The valve was found to be closed as far as it would go, and evidence showed that it had not been opened accidentally : it was found, however, to leak slightly under a pressure of several inches of water. While the fan was working this defect in the valve did not result in the entry of gas into the pan and the test indicated safe conditions.

This accident is typical of many that illustrate the absolute necessity of completely disconnecting, and blanking off, from all possible sources of dangerous gas, any plant that is to be entered. No other precaution can take the place of disconnecting and blanking off. A spectacle valve, properly bolted with a made joint, is a form of disconnection and blanking. Incidentally, although reliance on the use of mice was not the cause of this accident, it should be appreciated that mice are not safe indicators except for carbon monoxide and hydrogen cyanide. Chemical tests should be used wherever, as in the case of hydrogen sulphide, reliable tests have been devised.

Even when a vessel has been thoroughly purged with steam and air and has been completely isolated from every possible source of dangerous fume, and the atmosphere inside it has been tested and shown to be safe, that vessel may still be unsafe to enter without breathing apparatus and a life-line. It may be unsafe to enter if it contains sludge. During the last war a process for the cleaning of tanks attracted the attention of people who had to concern themselves with this problem in marine and land transport and in factories like chemical works. The process depended upon the treatment of the tanks with carbon tetrachloride. Hot carbon tetrachloride vapour from a special portable boiler was injected into the closed tank. This dissolved the tarry deposits on the inside walls of the tank, and, after a suitable number of injections had been given, the solution of the tarry material in the condensed vapour was discharged through the cock at the bottom of the tank. A railway tank-wagon, that had been treated in this manner, was left with the top manhole and the bottom cock open for nine days. The atmosphere was tested at intervals and on the ninth day, when the test indicated that the atmosphere inside the tank was safe, a foreman entered. He could smell no vapour. The next day a workman entered and removed some of the tarry sludge that remained on the bottom of the tank. On that occasion he was unaffected. Two days later, the tank having remained open in the meantime, he entered again and continued the removal of the sludge. After he had been working for about an hour he was overcome by the fumes which no doubt were released from the sludge that he was disturbing.

This was not a fatal accident ; the man recovered. The story has not been introduced because of any disastrous element in it, but because it provides a good example of the unpredictable and insidious behaviour of sludge. Many fatal accidents have occurred, however, because of the presence of sludge and scale. In one instance acid was used to decompose sulphides in a process for the extraction of iodine from seaweed. Some of these sulphides were present in a crust that formed on the top of the liquor. Most of the liquor was discharged from the tank and, after ventilation for a number of days, the atmosphere inside it was tested and found to be safe. Two men then entered to clean out the residual sludge. In doing so they disturbed the crust containing the sulphides and caused it to come into more intimate contact with the remaining acid whereby hydrogen sulphide was liberated. Both men were killed and men standing outside in the vicinity of the tank opening were overcome. In another instance two men, who were cleaning scale from the inside of a petrol storage tank, died from the effects of lead tetraethyl in spite of the fact that the tank had been positively ventilated for months before entry, and the air inside it had been tested with great care.

Warned by such accidents, the factory inspector considers that the presence of sludge or scale calls for precautions, in the form of breathing apparatus and life-lines, that are no less thorough than those required in the case of the presence of the dangerous gas itself.

Explosions

During the past twenty years the attitude of people, who have had to concern themselves with the problem of explosions on industrial plant, has changed very considerably Previously the general tendency was to make an exhaustive study of the possible sources of ignition—a most necessary undertaking—and to support precautions based on that study by a few additional precautions, which, although useful in themselves, did not play a part in any systematically planned general scheme. Nowadays increasing attention is being paid to the avoidance of flammable concentrations when the substance is capable of forming explosive mixtures with air, and to precautions aimed at limiting the spread and effects of an explosion. The next three accounts are typical examples of the severe education we received on the subject of dust explosions.

Examples and their lessons

In a provender factory cotton-seed cake was being ground in a mill in the basement of the building, and the ground material was being carried by a bucket elevator passing through several floors to the bins at the top of the building. The ground material was ignited by some means, perhaps by the friction set up by a bucket of the elevator that was later found to be loose inside the casing. A dust explosion took place inside the elevator and the casing was burst in a number of places. The investigation seemed to show that no one was injured by the primary explosion in the elevator. But there were accumulations of loose dust in the rooms through which the elevator passed, and the explosion in the elevator dislodged this loose dust, giving rise to dust-clouds in the workrooms. Flame from the burst elevator casing ignited the dust-clouds and a secondary dust explosion spread throughout the factory. The building was wrecked, six people were killed in the secondary explosion, and a large number of people was injured.

The lesson to be learnt from such explosions is the disastrous character of a secondary dust explosion in the workrooms and the vital necessity of avoiding the possibility of inflammable concentrations of dust in the workrooms. In other words, we have learned to appreciate the necessity for the exercise of scrupulous cleanliness to prevent the formation of accumulations of dangerous dust in the workrooms.

In a somewhat similar secondary explosion in a cork mill the explosion spread from one room to another and indeed, by communicating galleries and enclosed bridges, from one building to another. Five men of a reduced night staff were killed by this explosion.

The previous lesson was confirmed and additional evidence was provided of the need for effective separation of workrooms and buildings to limit the spread of the explosion.

The manufacture of fine metal powders, such as those of aluminium and magnesium, has been associated with many disastrous dust explosions. The following account of a magnesium dust explosion is not being given as an example of an explosion that had disastrous consequences : it has been included because the explosion in question played a considerable part in establishing the attitude that should be adopted concerning the precautions to recommend for the manufacture of aluminium and magnesium powders, and in confirming the views already adopted concerning dust-settling plant in general such as cyclones, bag-filters, and settling chambers. The plant that was associated with the explosion consisted of a hammer-mill with a coupled fan for the pneumatic conveyance of the ground material, a separator for over-size material, and three cyclones arranged in series in such a manner that the coarsest material was settled in the first, the medium-range material in the second, and the finest powder in the third. Originally the cyclones were installed inside the building, but, some time before the explosion occurred, the firm had transferred them to a small yard outside. During a meal interval, while the mill was running under the supervision of the only workman remaining on the premises, an explosion occurred on the plant which caused the complete disintegration of the third cyclone, wrecked the second, and considerably damaged the first. The workman was not near the cyclones at the time and he escaped with very minor injuries, but surrounding buildings were damaged. If at the time of the explosion the cyclones had still been inside the building and men had been working there an explosion of this violence would have been disastrous.

This explosion provided impressive evidence of the unusual violence that is associated with the explosions of certain metal powders and dusts. Subsequent explosions and experimental work confirmed this evidence. It was realized therefore that precautions for the manufacture of such powders would have to be particularly severe. In one or two instances successful arrangements were made to avoid flammable concentrations by the use of inert gas. But in the great majority of processes the possibility had to be accepted that an explosion could occur. To ensure that the people working in the factory would not be injured by the explosion, the plant on which an explosion could occur had to be housed in strong cubicles with explosion reliefs relieving to the open air. The doors giving access to the cubicles had to be strong doors interlocked with the drive in such a manner that the cubicle could not be entered while the plant was running. The process was controlled from outside the cubicle. Sometimes certain parts of the plant could be situated in the open air, in a safe place that could not be approached while the plant was running. In such a case the controls were usually operated on the safe side of a strong wall inside the factory.

The precaution of isolating dangerous plant from occupied workrooms has been applied to plant in which explosions other than those of metal powder are liable to occur. It is known that explosions in settling plant, like cyclones and bag-filters, can be particularly violent, and it has become a practice to urge that such plant be installed in the open air or be otherwise isolated from the workroom.

Experience has shown that bucket elevators inside a factory can be similarly dangerous, and they have the added danger, that, since they generally pass through a number of floors, they can start simultaneous, secondary explosions in a number of storeys of the building. It is good, safe practice to install them in a separate tower on an outside wall of the factory building or to replace them by safer types of elevators.

Fire and explosion

The danger of fire and explosion associated with flammable liquids and their vapours has been well appreciated and it has for long been customary to take certain precautions. For example, it has been the practice to provide bund walls round storage tanks to retain flammable liquid in the event of spillage and to prevent it from flowing to a place where it could become ignited and cause a serious fire in the storage area. Storerooms have been provided with raised sills at doorways to serve the same purpose. It has not been so readily recognized, however, that similar precautions are required for flammable liquids in actual use in the process. Sometimes the quantity of liquid present at any time in the process plant is as great as that present in a large store. It may be present at different levels in the building, and, in the absence of precautions, a serious leak may endanger the whole factory and the people in it. This observation is so obvious that no one would seek to deny its truth, yet it has been remarkably difficult at times to convince those responsible for such plant that precautions were needed to prevent the spread of spilt liquid in process similar to those provided for liquid in storage. Indeed difficulty has been experienced in dissuading a company from using open chequer plate flooring in a multi-storey building in which large quantities of flammable liquids were used at different levels in the building.

The danger resulting from the spread of spilt flammable liquid from a process vessel is exemplified by an explosion that occurred in a factory in which flammable solvent was used in an extraction process. A tank containing extracted material in solution split at a seam and liquid poured out on to the floor of the room. There were no arrangements to prevent the liquid from spreading and it spread through doorways and through openings in the floors to lower levels of the factory. **In** the meantime the air of the workrooms was becoming charged with flammable vapour which was soon ignited. In the explosion that ensued twelve people were killed.

After this accident, opinions that were held concerning the necessity for kerbs and sills to restrict the spread of spilt liquid from process vessels became convictions. When new-plant is being installed for processes using flammable liquids, the arrangement of the plant and the design of the building should be such that retaining kerbs may be provided without impeding normal movement and activities in the vicinity of the plant. With the development of modern methods of remote control, however, it is becoming increasingly possible to construct in the open air plant that had hitherto, in the interests of the workers' comfort, to be inside a building. This tendency is likely to bring about a considerable reduction in danger from fire and explosion.

The last example to be considered relates to a situation so frequently associated with bad accidents that great emphasis has had to be placed on the precautions. When a vessel has contained a flammable material and heat is to be applied to it for some purpose such as welding, brazing, soldering, or cutting, any flammable mixture that may be present in the vessel or that may be formed as a result of the application of the heat is almost certain to be ignited. Many fatal accidents have occurred from explosions caused in this manner. In one case a man had been instructed to cut open a drum that had contained a solid flammable ester—a waxy material. While he was cutting the steel bands round the drum, the heat of his torch caused residual material sticking to the inside of the drum to vaporize. By the time he had cut off the top of the drum an explosive concentration had formed inside the drum, and this was ignited by the flame of his torch. The man was killed by the explosion.

Before an operation of this sort is undertaken one must make certain that there is no flammable concentration inside the vessel, and that a flammable concentration cannot develop in the course of the work. To make sure that this is so, every trace of flammable material must be removed from the vessel. Sometimes it is sufficient to purge the vessel thoroughly with steam, but, when heavy oils and greases are present, the vessel may first have to be boiled out with alkali and then steamed. If there is any doubt concerning the adequacy of the treatment that a vessel has received, a test should be applied.

Conclusion

Accidents such as those described above have led the Factory Inspectorate to place special emphasis on certain precautions, but it should be unnecessary to add that these precautions arc not emphasised to the exclusion of all others. To deal with all these, however., a much longer account would have to be written.

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