DISCUSSION

Dr. C. A. CURTIS said that usually the hazard of explosion was expressed as an " explosive range ". For instance, in the case of hydrogen–air it was 6·4–75%. The lower limit in the case of oil mists was lower than that for hydrogen–air but an upper limit was not given. Burgoyne expressed the hazard in droplet size which could not be controlled in the case of gases. Could he give a definite upper limit for the explosive range of oil units?

Dr. BURGOYNE replied that he had spoken of the lower limit of concentration below which there was no hazard and above which, there was. There was certainly an upper limit and a number of references were made to it in the paper. It was difficult to define in experimental work, however, because there were common situations where part of the suspension was more concentrated than another part and there was a very wide range of overall concentrations where flame propagation through part only of the mixture occurred. The upper limit could not therefore be defined at all effectively in the laboratory and he felt that that was, in fact, the situation that would occur in practice.

Therefore any laboratory results that might be obtained would have very limited application.

Dr. W. E. F. NAISMITH asked about the effect of water vapour: would the absorption methods for determining mist concentrations be applicable only where the system was a dry one? If water vapour was present, did it interfere with the method of measurement? He was referring to a suspension where there was condensation of water vapour as well as of oil.

Dr. BURGOYNE replied that water vapour would be an embarrassment in practical situations where an attempt was being made to assess the mist concentration by a method of filtration. Some liquid water might be collected on the filter and a misleadingly high weight-to-volume ratio obtained. The same would apply with optical density instruments. If there were condensation of water vapour along with the fuel it would give a misleadingly high reading.

Dr. NAISMITH asked if the methods were therefore of limited application.

Dr. BURGOYNE said that, if used as a warning device, an unnecessarily large margin of warning would be given, but if exact methods were being used, the figures would be invalidated.

Mr. N. GIBSON asked how sensitive the mists were to ignition by an electric spark discharge. Was there any relationship between the minimum spark energy required to ignite a solvent mist in air and the corresponding vapour–air mixture?

Dr. BURGOYNE replied that there was probably not much difference between the ignitability of the mists of very small drop size and that of the corresponding vapour, but the matter had not been precisely investigated, and only incidental laboratory experience of igniting both kinds of system was

available. The sprays, with larger drops, would be distinctly more difficult to ignite than a vapour or gas–air mixture.

Mr. K. N. PALMER asked whether Burgoyne considered that the values of the lower limits for flammability would change with the diameter of the tube in which they were measured? In the wider diameter tube particularly, would the effect of radiation between the droplets affect the values obtained for the lower limits?

Dr. BURGOYNE replied that he was not entirely happy about the diameter aspect of the measurements with sprays of intermediate or large drop size. The question was whether the flames were unduly quenched through not using large enough tube diameters in the tests. The possibility was that, with larger diameters, the limits might be a little lower because of the reduction of the quenching effect. The criticism was a valid one, but the effect of correcting for it would, if anything, be increased flammability and increased difficulty of suppression in the intermediate drop size range of 100 to 200 microns.

With regard to mists of drop size of 10 microns or less, he did not think there would be a significant correction. Experience with gases and vapours would indicate that the 2 in. tube he used was representative of larger ones.

Dr. G. A. CURTIS pointed out that Burgoyne had indicated that hazard could be reduced by dilution with nitrogen or carbon dioxide and asked whether water vapour could be used successfully since the two gases were not suitable in workshops. How much moisture would be needed?

Dr. BURGOYNE replied that the effect of water vapour would be intermediate between the effects of nitrogen and carbon dioxide and would run parallel with them.

He did not see why the use of water should not be practicable. It might operate either as a vapour or as a condensed mist if cooling took place, when there would be a mixture of water droplets and fuel droplets. If the condensed water mist were in the low drop size range, as it would be by the process of natural condensation, the effect should be equivalent to that of the water vapour. With a small drop size, vapour and mist were equivalent in effect. That should apply to the suppressant as well as the fuel.

Mr. O. G. WELLER asked whether, in dust explosions, there was an optimum particle size as for liquid drops suspended in air.

Dr. BURGOYNE replied that he would have thought so but, so far as he knew, this had not been shown. Experimentally, the subject was difficult and he was not aware of practical investigation which showed that effect with solid particles.

Mr. Z. W. ROGOWSKI referred to the question of venting when design pressures were very low, and the enclosure large. Swedish work with an enclosure of 7000 ft^3 showed that maximum pressures were not caused by combustion inside the vessel, but outside, and pressure waves arriving at the gauge inside the enclosure determined the maximum pressure. That was another difficulty encountered when venting at very low maximum pressure.

There was oscillation which gave considerable pressures, perhaps a factor of 70.

All sorts of effects came in, in the troublesome region below the levels of design.

When designing the vent systems for ducts, one had to design for very low maximum explosion pressure. With such vent systems quite often loose or magnetically held vent closures were used, and with these frequently the maximum explosion pressures were determined by the weight of such closures. There are examples of many difficulties in attempting to formulate a vent design data that could be applied widely.

Dr. MUNDAY replied that under conditions of supersonic flows through ducts, the weight of the cover had less effect. For low pressure venting, the weight of the duct was of considerable importance. In the cases he had prepared, the initial pressure in the vessel was 15 lb/in² gauge. The pressures were being doubled and trebled and even multiplied by six before the vent opened.

He had purposely neglected any pressure fluctuation. In order to calculate that an equation for momentum had to be included.

Mr. N. P. T. PHELPS said that the theoretical work discussed concerned explosion through burning gas. Was the same analysis applicable for gas release?

Dr. MUNDAY replied that it would not be applicable for pure gas release. It was fairly well established that in simple venting the pressure reduction was in fact a function of the volume of the vessel. He did not see how a constant pressure could be achieved in pure gaseous discharge and, since that was the criterion for the "safe" venting area, the results would not be applicable.

Mr. R. TINSON asked whether the allowances for turbulence would still be applicable if the theory were being applied to very large volumes, for example the cargo spaces of tank ships.

Dr. MUNDAY replied that there was some hope of the applicability, even to fairly large vessels, but only if the pressure were such that the flow was supersonic. Only a slight modification of the theory was needed to make it available for the subsonic flow conditions but this complicated the mathematical treatment and factors such as vent cover weight, friction along ducts, etc., became important and had to be taken into consideration.

Dr. D. J. LEWIS asked Munday if he had carried out an assessment of the work of Cousins and Cotton with regard to hydrogen–air explosions and if he felt that his formula giving safe venting areas would be applicable for very fast explosions such as for hydrogen–air. Considering the experimental work of Cousins and Cotton, the maximum explosion pressures were very considerably higher than the bursting disc pressures in all cases.

Dr. MUNDAY replied that one of the difficulties of the work of Cousins and Cotton was the type of evidence required to establish the effects of venting. The term Hbn was difficult to establish for hydrogen–air mixtures and secondly, Cousins and Cotton in that series of work had not mentioned where the ignition point was in the vessel.

(The calculations have now been extended to cover the hydrogen–air explosions by making certain assumptions and the results are included in the paper.)

Dr. LEWIS said it would be interesting if Munday's assessment enabled predictions to be made based on experimental results with one gas mixture, of what could be expected to occur with another gas mixture. This problem seemed to present itself a great deal at present in practical applications of explosion relief.

Dr. MUNDAY replied that one was again merely concerned with the value of H; the values of b for the work reported by Cousins and Cotton correlated very well with his own formula.

Mr. P. GRANTHAM asked if there was any known incidence of accidents from laboratory-scale operation using the materials described by Munn.

Dr. MUNN replied that one or two cases of bladder tumour had been known to occur in persons whose sole contact with the materials had been in the laboratory. It was impossible to prove whether or not such contacts had been responsible. He thought it could be said that ordinary laboratory use of such materials did not constitute a serious hazard, but not that such use was free from hazard. Benzidine had been used for many years in medical laboratories, but tolidine was now used instead.

Mr. T. SUTTON asked what the net total suffering annoyance or inconvenience to the human race would be if the manufacture and use of these chemicals was totally abandoned.

Dr. MUNN replied that there would be some inconvenience but little suffering. Certain derived products could not be replaced; for others there were suitable alternatives, but more expensive. The only way in which world-wide abandonment of bladder carcinogens could be achieved was probably by international conventions. There were other carcinogenic processes used in industry, such as ionising radiations. It would not be in the interests of mankind to abandon that sort of work.

Dr. V. D. LONG asked what quantities of carcinogens were involved in the formation of papilloma of the bladder.

Dr. MUNN said he thought that no quantity of carcinogen was too small to be considered dangerous. It was not possible to establish an upper limit of safety. All carcinogens were not equally hazardous—alpha-naphthylamine was much less dangerous than benzidine, which again was much less dangerous than beta-naphthylamine. He had no doubt that alpha-naphthylamine could be made and used safely. He was doubtful about benzidine. Its manufacture still continued in America and on the Continent, but he was not in a position to say if it was being made safely. He had no doubt that beta-naphthylamine could not be made safely, certainly in a plant subjected to normal commercial pressures.

Dr. C. A. CURTIS said that benzidine salts had been mentioned; there was surely a big difference in the toxicity of the base versus the salts? The hazard would be less with salts than with the base.

If benzidine was made in an enclosed plant, entirely isolated, and was produced in the form of a hydrochloride slurry it was fairly safe.

Dr. MUNN said that he did not wish to be misunderstood. When he had mentioned benzidine, he included as being dangerous both benzidine base and any of the salts of benzidine. Benzidine dihydrochloride was safer than benzidine base only by virtue of its much lower vapour pressure. It could be absorbed through the skin in the same way as the

base, and in that way benzidine dihydrochloride constituted a great hazard. He agreed that it was safer as a slurry than as a dry powder or flake.

However, he believed that the true point that the questioner was trying to make was that, if benzidine were made in an enclosed plant, and reacted *in situ* without being discharged, then the hazard had been eliminated. That was largely, though not completely, true. The old problem of maintenance still existed, and enclosed plants containing benzidine had to be opened up for that purpose.

Mr. J. D. MITCHELL said that he was interested in three materials—triethylamine, its hydrochloride, and its acetate. He asked if any hazard of the type under discussion was associated with them?

Dr. MUNN replied that triethylamine and its salts were free from carcinogenic hazard, though triethylamine was dangerous in other ways. It was the aromatic amines which were bladder carcinogens—although not all of them—and the aliphatic amines were not carcinogenic. Some experimental carcinogens were of little importance industrially.

Mr. P. GRANTHAM said that he was very interested in the subject of TDI and he referred to Corbett's figure of 0·1 ppm. He asked if Corbett was aware of the recent reference in the *American Journal of Hygiene*, suggesting that some people were affected by 0·1 ppm and that 0·02 ppm should be the maximum allowable concentration.

He also asked what was the sensitivity of the two-minute tests for TDI. The method used by his establishment took 20 minutes for sampling time, and several hours of laboratory time.

Mr. CORBETT replied that the TDI analyser could get figures down to about 0·01 ppm. It measured in a similar way to that of most other equipment. A measured amount of a gaseous fluorinated hydrocarbon was passed through the apparatus, which sucked in an equivalent amount of air. *Iso*cyanates present are converted into a dye solution and the colour intensity measured. It was very sensitive—much more sensitive than some of the more elaborate and lengthy processes in use at the present time.

The value of 0·02 ppm suggested was possible to achieve. The difficulty might be the ability to analyse accurately at such a low level. He thought that it could be done with the analyser, but it was rather a doubtful figure.

Dr. A. MUNN said that he wished to make some observations as one who had, as a major interest in life in the past few years, been concerned with medical effects of *iso*cyanate. It was quite true that the American Conference of Industrial Hygienists in 1961 lowered their recommended maximum allowable concentration from 0·1 ppm to 0·02 ppm, and in the United Kingdom, last year, the Ministry of Labour, in their document which recommended maximum allowable concentrations, followed suit; so that, in Britain, so far as the Ministry of Labour and the Factory Inspectorate were concerned, the maximum allowable concentration for toluene di*iso*cyanate was 0·02 ppm. It was possible to measure down to that low limit, not lower.

In addition to the device described by Corbett, a piece of equipment, which was not expensive, had been manufactured in America by the Mines Safety Appliances Company. It was simply and easily operated; it could be operated by an unskilled worker with only a few hours' training, and it gave reliable results. He would not suggest that it was necessarily possible to use it at concentrations as low as 0·02 ppm and below that figure throughout an entire working day, but he

had no doubt at all that it was possible to get down to a level which would average less than that over a working day.

Of all the new materials which had appeared on the industrial scene during the last 10 years, none was more interesting medically than toluene di*iso*cyanate. As Corbett had said, its use was increasing all over the country and, in fact, all over the country there had been reports of cases affected by TDI. The cases had occurred all over the country not because it was impossible to use TDI safely; it could certainly be used safely, but because the difficulties of using it safely had not been fully appreciated. The technique of its use was very different from that of most other compounds, as was the extent of the care necessary. It was very often difficult for a light engineering company—and *iso*cyanates were, for example, used in the manufacture of refrigerators—unaccustomed to toxic hazards, to comprehend the degree of care necessary. Difficulties arose in the conception of the nature of the hazard. Everyone was accustomed to hazards where there was an arithmetical relationship between the degree of the exposure to a noxious material and the severity of the symptoms which subsequently appeared. If a man got a large dose of chlorine, he would be very ill and might die; if he got a moderate dose, he would be made moderately ill; if he got a small dose, his chest might be affected slightly, and if he got just a whiff, he might not be affected at all. When sensitisation to *iso*cyanates occurred, such was not the case; there was no arithmetical relationship at all between the degree of exposure in a sensitised individual and the severity of the symptoms that might develop. In an atmosphere where a normal person might work safely and happily all day and everyday, a person who was sensitised, who had developed an allergy, might well be affected after being there for only a few minutes; nothing could be smelt and no ill effects experienced except by the unfortunate sensitised individual.

Mr. N. P. PHELPS asked if there were any special hazards in using polyurethane or its derivatives for making foam lagging when Freon was used as a carrier.

Mr. CORBETT replied that polyurethane was physiologically inert; this was a general property of all macro molecules. Although they started off as a monomer quite dangerous in many respects, the macro molecule which resulted from it was physiologically inert, so there was no danger at all.

Dr. V. D. LONG said that the maximum concentration referred to the 8-hour day and the average concentration; was there any information about the peak values which could be tolerated for short periods? With regard to ventilation, Corbett had said that the vapour was heavier than air and that 70% of the extraction was downward; why should not all the ventilation be downward?

Mr. CORBETT replied that the vapour was six times as dense as air. If the chemicals used in urethane reactions were considered, TDI—which had a high vapour density—was principally used. Other chemicals, with lower vapour density, were often used, which came off as vapours in such reactions. They might not all take part in the actual chemical reactions. Because they were volatile and the reaction was highly exothermic, vapours from those additional chemicals were also given off, making it necessary to extract both top and bottom. Not many people did low-level extractions. The ideas given in the paper were those which suited the particular reaction discussed. Most people used overhead extraction completely, but it was a function of design, and the number of people involved in the urethane industry at present was relatively small; ideas took quite a time to develop. The

mechanical development of the industry was quite a long way behind the chemistry but it should be coming along now.

He did not know what the figure for peak values would be; he was completely insensitive to TDI so he could not really tell.

Dr. A. MUNN said that he could throw a little light on the problem. At about 0·2 ppm, the average individual could begin to detect TDI through a sense of slight discomfort in his eyes and nose and throat. As the concentration went up, to 0·3 and 0·4 ppm, the discomfort became increasingly unpleasant and the normal person was reluctant to remain in such an atmosphere. If he did, at that level he might well experience some slight tightness of the chest thereafter, but was not likely to come to serious harm. If it became as high as 1 ppm, he thought that any persons exposed to such a concentration for more than a few minutes might well have moderately unpleasant symptoms afterwards. A person who was sensitised could not tolerate any measurable concentrations at all. In fact, cases had been seen that were so sensitised that it was felt that even the odd molecule was apt to produce quite an unpleasant effect.

Mr R. J. KINGSLEY said that he was a little disturbed about the cell explosions from the point of view of further secondary explosions being initiated, in the call room or elsewhere. Was there any possibility of that occurring with the plant described by Pennell?

Dr. PENNELL replied that he knew of no occasions where that had occurred. The chlorine usually left a cell with the weak brine; a quite large flow of brine left the cell with the chlorine, which would help to prevent the explosion spreading into the chlorine collection main. He had heard of an incident in Germany where an explosion occurred in the main itself, but it apparently occurred at some point along the main and was not caused by a cell. It was not initiated by a cell explosion. There was another incident where a mild explosion occurred in a chlorine drying tower, but he knew of none that had been initiated in a cell itself and carried into the chlorine collection system.

Mr. D. M. MacLAREN noted that in dealing with electrical hazards Pennell had concentrated mainly on direct current as the source of hazard. His own experience, however, indicated that much more severe trouble could develop if there were a leakage of alternating current onto the direct current system. It was common practice to run auxiliary alternating current circuits such as mercury pumps at very low voltages, about 40 volts 3 phase. It was also desirable to operate these auxiliary electrical systems as un-earthed systems.

Mercury vapour could condense on the walls of buildings and might re-vaporise at a later stage, causing further trouble. Some cell rooms were tile-lined on the walls as well as the floors, so that they could be washed down. He knew of a cell room in the Continent of Europe in which, after many years of operation, mercury had percolated through the concrete floor to such an extent that when the building was demolished, some tons of mercury were extracted from the sub-soil.

A SPEAKER said that he wished to know more about the electrical control gear associated with the pumps in the cell room. Hydrogen was a Group 4 gas and no certificates for electrical control gear had yet been issued for Group 4. A certain range of motors had been certified, although he was under the impression that it was essential they were blown to fresh air.

With standard industrial control gear away from the danger zone, he thought that it was an essential, which he felt would not be waived by exemption 4, that an emergency stop button had to be placed alongside each drive, as nothing was certified. What practice was adopted by Murgatroyds to overcome the difficulty?

Dr. PENNELL replied that the mercury flow could, at any time, be stopped and a cell put out of operation quite easily by pressing a button. He was not sure about the particular type of electric motor used. However, the hydrogen fire risk was not normally great, although, of course, fire precautions had to be carefully observed.

A SPEAKER said that there was no normal flameproof equipment used in cell rooms in the United Kingdom nor abroad, to his knowledge. He did not know about the motors at Murgatroyds but in the cell line he knew, the motors were not flameproof nor intrinsically safe; they were not certified. The argument was that the amount of hydrogen escaping from a cell was small; air changes were moving so rapidly that the hydrogen escaped quickly to the roof space in the building and should go right out. It was argued that it was virtually impossible to get an explosive mixture of hydrogen in air at or about cell level.

The problem with which he had been concerned was the lighting fittings in the roof, but even so, in all countries, it was common practice to use orthodox electrical lighting actually in the roof space, as the hydrogen should, by that time, have dispersed in such a large volume of air that it was well outside the explosive limits. The fittings used in the roof spaces should not be so arranged that, by heating and cooling, they could draw hydrogen in and build up a concentration of hydrogen inside the fitting. Hence, the tendency was to use very open fittings.

A SPEAKER said that hydrogen was used in some of his company's operations and their electrical equipment was all pressurised. All electric wires were run through a conduit which carried air under a slight pressure, and all lighting fittings in the roof were pressurised.

Dr. V. D. LONG said that it appeared, from Pennell's paper, that titanium was an excellent metal to use for corrosion resistance. In an earlier session it had been shown that intense sparks could be produced from titanium; did that introduce a further hazard?

Dr. PENNELL replied that he had pointed out one of the dangers, which was that with very dry chlorine, if it contained less than 0·015% moisture, there could be spontaneous ignition. No trouble had yet been experienced with the titanium installed and he had never heard of any fire due to titanium ignition in wet chlorine. He had said that titanium was an excellent material for use with wet chlorine and chlorinated brine, but he had made the point that some electrolytic corrosion of titanium had been experienced when it had been used as an orifice in the brine feed, in a diaphragm cell installation. The occurrence was recent and there had not yet been an opportunity to investigate it fully.

Mr. Z. W. ROGOWSKI asked how the figure of more than 100 ft. had been arrived at by Wade for the hydrocarbon discharge stack.

He was interested also in the inversion conditions.

Mr. WADE replied that the height of 100 ft had been chosen in order to avoid downwash from buildings and because it satisfied the formulae in fairly still air conditions.

Inversion conditions occurred because the surface of the earth lost temperature after sunset but the inversion layer did not normally exceed 100 ft. The way to overcome inversion was to emit the gases at high velocity. API 520 mentions very high velocities of discharge, 500 ft/s, and it is often not difficult to achieve this. When the velocity was increased, jet mixing and dilution occurred.

Dr. M. RUHEMANN said that he presumed Wade was referring to plants which were actually designed by I.C.I. Were the design features which involved safety—not the features for avoiding a hazard after the plant had been designed—incorporated by the process design engineers themselves or brought in by specialists who were allotted to the design team during the design period?

Mr. WADE said that the particular plant he had described had not been designed entirely by I.C.I. but the specifications had been drawn up jointly with a contractor. Invariably detailed specifications incorporating safety features, were drawn up by I.C.I. before detailed design commenced. In the case of a new process a great deal of advice was taken from hazard experts who conducted experiments during the research and development stage. In the case of well-tried processes a great deal of advice came from experienced process operators who were seconded to the design team.

Mr. D. CONNER asked why Palmer used horizontal propagation of flames from the ignition source, when the most severe industrial case likely to be encountered would be upward propagation from the ignition source?

Mr. PALMER replied that the main reason for using horizontal propagation with a long piece of pipe was that it was easier experimentally to do it that way. Some experiments had been done with vertical tubes up to about 6 ft long and the flame speeds were not very different. Where there was flame propagation and not detonation, if a series of experiments were done under identical conditions, the flame speeds varied over a range. If the largest value of flame speed under horizontal conditions was taken, it covered most vertical flame speeds as well. If a particular installation were vertical, and there was much concern about having a flame trap which would only just do the job, additional tests might have to be done. But because of the variation in flame speed, a safety factor was generally used which would cover the slight difference in flame speed between horizontal and vertical propagation.

Mr. CUBBAGE said that some of his experimental work had been done with vertical propagation and although the flame velocity had, in fact, been increased, the detonation velocity was not changed. This work had been reported by him.[1]

Mr. A. J. A. VAN DER ZIJDEN asked if there was any information on the testing of water seals installed for preventing flame flashbacks into flare-stacks. API recommended[2] the application of water seals and stated that water seals were more reliable than crimped-ribbon flame arresters or gravel pots. He could not, however, find any information in the literature about the testing of water seals.

Mr. PALMER replied that very little work had been reported on the testing of the water seal type of arrester for large-scale plant. The arrester consisted of a sealed tank of water through which the gas bubbled in normal operation. An explosion or flashback entered the space above the water and the water was forced back up the inlet pipe, and sealed off the rest of the plant.

The first point about the water seal arrester was that it had to be a substantial piece of equipment in order to stand the explosion pressures. Secondly, the water had to be kept at the right level. Thirdly, there should never be a continuous path back through the gas up into the inlet pipe.

Water seal arresters were used on a smaller scale for acetylene explosions where acetylene was being piped in a narrow bore tube. They were satisfactory under such conditions for stopping acetylene detonations.

The general advantage of water seal arresters was that they would not block up if the gas coming through was dirty. Sludge would form in the tank. The disadvantage of these arresters was that they were relatively large and needed to be strong enough to withstand the explosion pressure.

Mr. VAN DER ZIJDEN asked what provision I.C.I. made for preventing flashback.

Mr. J. L. HOPKINS said that they had no flame arresters in the blow-down lines to a flare-stack.

Material being blown down inevitably contained constituents which would quickly block the passages of a conventional flame arrester. However, a water seal was provided at the base of each flare-stack for warm blow-down gases and, as a further general precaution, a limited amount of inert gas was released continuously into the stack. With stringent attention also on the part of operators to the exclusion of air, these arrangements should prove effective in preventing flashback of flame from the pilot light at the top of a flare-stack into the blow-down system.

Mr. VAN DER ZIJDEN said that the only question was that of flame coming through the top of the stack and, in fact, steam was put in the bottom to stop that.

Mr. J. L. HOPKINS said that he assumed that the questioner was concerned, as had been the lecturer, with plants in which oxygen was not present as a necessary participant in the process. In these circumstances their object in design and in operation was to ensure that all air was effectively purged out on commissioning, either of the plant as a whole or of individual items of equipment, and thereafter was kept out. It was usual to have a controlled bleed of inert gas into the blow-down system and there was also, of course, a degree of involuntary leakage of hydrocarbons past relief valve seats and so on. Their experience suggested that, under these conditions, a water seal was an adequate flame trap. The other purpose of the water seal at the base of a flare-stack was to condense the heavier constituents of the warm blow-down, the presence of which would make out of the question the use of a conventional flame arrester.

Mr. Hopkins said that the flare-stacks he had in mind were typically 30 in. in diameter and some 200 ft tall. While air might, under certain conditions, diffuse back into a flare-stack, the continuous flow of inert and other gases from the base would limit penetration. It should be remembered also that ignition occurring in such a situation would be from an open end and the pressure build-up consequently small. He felt that, in those circumstances, the likelihood of a hazardous situation arising from back-flow of air into a flare-stack was extremely small.

Mr. P. L. KLAASSEN said that, although in normal operation, oxygen would not enter the flare system, under misoperation, oxygen might get in. He had experience of flares which produced a vacuum and if there was a leak, oxygen got in. Wade was speaking of normal operation but effects should be considered at start-up, shut-down, maintenance and misoperation. Would Wade agree that an area that had been declared safe during discussions in the plant design stage might prove to be a danger spot due to the fact that things did not go as imagined during design, and conditions changed. The flare-stack looked, from the photographs, as if it was positioned in the centre of the plant. Was that so?

Under normal conditions, the columns operated at very pleasant temperatures; when shut down and depressurised, there were unpleasant, low temperatures in the equipment and in the venting lines, blow-down lines, etc. How was that dealt with? Had special materials been selected for it?

Mr. WADE replied that in the plants described the flare-stacks were not in the centre of the site but had been situated in or near the furnace areas where there were already naked flames. Naked flames had to be segregated from dangerous materials so the flare-stack and furnaces had been confined to one end of the site. In fact a boundary fence some 150 ft square was erected around the base of each flare-stack and personnel and equipment were normally kept outside that area.

Special precautions were necessary to ensure that a process which had been working satisfactorily on routine for fifty-one weeks in the year did not constitute a hazard on the fifty-second week when it had to be shut down for inspection and repairs.

Depressurising the unit necessitated the flaring of considerable quantities of hydrocarbons since inventories of liquefied hydrocarbons are vaporised or moved to safe storage.

Care must be taken during those operations not only to control the amount but also to avoid chilling the equipment below its design figure. Inert gas was admitted continuously during that stage to prevent entrance of air, to keep the internal pressure close to atmospheric and thus prevent collapse from vacuum, and finally to remove residual hydrocarbons from the system. The purging with inert gas continued until tests confirmed the absence of dangerous gases. It was only by detailing the procedure, adequately catering for that procedure and seeing that no deviation was allowed that safe shut-downs and start-ups were assured.

Areas considered safe during the design could become dangerous under shut-down conditions, e.g. parts of the plant could be chilled, but by inserting insulation in the blow-down tanks, etc., sudden shocks on materials had been avoided. Carbon steel was used on the olefine units down to the limits of BS.1500, i.e. down to —50°C.

Mr. J. L. HOPKINS said that it was broadly their practice to use carbon steel at low temperature to the limits which had been shown to be safe by the work of the British Welding Research Association and of their own metallurgists. On static pressure vessels of wall thickness not greater than 1 in., and which it was practicable both to stress relieve and to hydraulically test, it was currently their practice to use ordinary grades of carbon steel down to —50°C with design stresses of 7 tons/in^2 or more. It would be appreciated that this went significantly beyond the recommendations of B.S. 1500:1958 and there was considerable hope that work now going on would soon show that a further extension in the use of carbon steel to still lower temperatures was acceptable.

At temperatures below —50°C it was generally their practice at present to use either austenitic stainless steel or aluminium alloys for both pressure vessels and process piping. However, they had used $3\frac{1}{2}$% nickel steel for pipes and pipe fittings at temperatures down to —90°C and were very interested in the possibilities of 9% nickel steel for pressure vessels at very low temperatures.

Dr. J. H. BURGOYNE commented on the water seal business. He said that the particular weakness of the simple type of water seal shown on the board might be that the explosion coming back into the sealed chamber would smash the dip tube—this had happened on some scales of operation—so by-passing the water seal. It would be advisable to apply explosion relief to the chamber anyway.

With regard to another type of water seal, the Acetylene Association of America had published details of a flashback arrester for acetylene, which was shown in the publication on a 4 in. pipeline. The device was some 6 ft in height. It was not actually a water seal arrester; it was so arranged that the gas in the normal forward passage passed over the water, but if the explosion came back the water was dispersed through the whole system into a dense cloud. It was claimed that

this suppressed an acetylene detonation. He was trying to find out the test by which this was established, but had not so far succeeded.

Dr. C. R. BLACK said that he was interested in the steam fences mentioned by Wade. They were new to him. He imagined that the use of steam must be very considerable. Could Wade mention figures and pressures used and describe the effectiveness of the device in different winds? How high were the fences and were they carried up just to the limit of the height of the plant?

Mr. WADE replied that if all the steam fences on the works were commissioned simultaneously the boilers would probably be flattened. They were not, however, used like that. Within the control room, there was a wind indicator and the process operators knew which section of fence would contain and dissipate a leak. In such circumstances, the usage would not be excessive. However, the main fences had never been used in an emergency to contain a gross spillage.

With regard to their height, the gas separation structure was 120 ft high and the ejector height was probably only 20 ft. The principle was that the heavy hydrocarbons which would settle near the ground would be contained by the brick wall and be pulled into the 10 in. diam. tubes by the ejectors. There they would be mixed with copious amounts of steam. They would be emitted with considerable velocity from the top of the ejector, and would be diluted with sufficient steam to make them innocuous.

Dr. J. H. BURGOYNE asked if any static electric effects were observed with the fences?

Mr. WADE replied that the answer to the question was " No ". The mild steel fences were of all-welded construction and properly earthed. Any static charge generated on them would leak immediately to earth. There was therefore no possibility of a separation charge building up to sparking voltage at the bottom of the fence where a dangerous gas–air mixture could exist. There was similarly little danger of a static spark occurring at the top and in this region the steam–gas mixture was safe.

Dr. V. D. LONG suggested that Wade elaborated the section on barriers because, in the paper there was no mention of ejectors, which appreciably altered the position.

Mr. M. SHAW asked Wade to elaborate slightly on the design considerations that ultimately decided whether a certain area was B or C or, equally important, C or D. It is useful to have the general criteria but the main problem is in reaching decisions. With a pump handling the solvent with a mechanical seal, it must be very much a matter of opinion of the individual designer whether the fact that there was a mechanical seal made it a remote hazard, qualifying for classification as area B.

Similarly, could Wade elaborate on the question of hydrogen? Theoretically, and taking hazard considerations to the absolute limit, the answer is probably not to use hydrogen. Unfortunately at times the gas had to be used and it was often used in conjunction with chemical plant. It is not uncommon to have hydrogenation vessels with drives and motors. He asked for elaboration on the decisions between areas B or C, or C or D.

Mr. WADE dealt with the easier question first: how to differentiate between D and C areas. There were some gases for which flameproof equipment was not safe (hydrogen was one and acetylene another) and where there was a possibility of those gases in an area that area became Class " D ". The best solution for such areas was to exclude all electrical equip-

ment and to use steam drives, for instance. Intrinsically safe equipment was permitted (for instruments) so long as it was designed safe for hydrogen, and another good way of dealing with the situation was to see that the hydrogen never got into any of the enclosures where the electrical equipment was housed. That was achieved by pressurising the enclosure, which could be a whole building or a metal box, depending on the extent of the electrical equipment. Normally nitrogen was used for small enclosures and a pressure switch was incorporated so that if a positive pressure from the inert gas did not exist inside the enclosure the electrical equipment was isolated.

With regard to decisions on whether an area was B or C, Mr. Wade admitted that some areas which were thought to be " C " some time ago were currently classified as " B ". As confidence increased in the ability of keeping areas safe from leaks of hazardous gases, so the number of " B " areas increased. A " B " area was located by a " B " source of hazard and in the paper that had been defined as a piece of equipment which had received a great deal of attention to ensure that as far as possible it was incapable of leaking.

It also had to be in the open air. There could be no " B " areas within buildings because if the area was not wind-swept a dangerous concentration could persist. Moreover, if there were a number of " B " sources of hazards concentrated in an area (e.g. a number of pumps all of which had reliable mechanical seals) the area might well be defined as category " C ".

Flameproof electrical apparatus could not be built for hydrogen, so the normal practice was to keep the area well ventilated; hydrogen being a light gas was easy to get rid of. It was no good putting a flameproof motor or other flameproof equipment, which had been designed for petroleum vapours, into a hydrogen atmosphere because the gaps in the metal-to-metal flanges were not safe for hydrogen and a gas-tight enclosure with a soft joint was a much better proposition. However, adequate ventilation or pressurisation to avoid a dangerous atmosphere was the solution.

Mr. P. L. CHARLESWORTH said that the presence of steam fences might be reassuring to personnel on the outside, but rather disturbing to someone on the inside. How was the decision made to bring them into operation? Did I.C.I. monitor continuously for hydrocarbons at selected points throughout the plant and did there have to be control of the movement of personnel inside the fences?

Mr. WADE replied that there were few operators inside the fire fences and they operated from control rooms. The control rooms were often very close to the low-temperature distillation units, to avoid travelling time, but the men in the control rooms were the ones who put the steam fences into operation.

There were parts of the plant in which a continuous MSA tester warned of dangerous conditions but that measure was used only in special locations, for instance where analysis instruments were housed in a building and hydrocarbon gases were taken through the continuous analysis instruments. In that case as well as the MSA warning device the building was swept with large air fans. There was also a continuous recording analyser on the tunnel going from Wilton to the Billingham site to indicate if there were any leaks.

Mr. R. BROWN asked if Cubbage or Palmer would comment on the possible use of crimped-ribbon flame arresters for acetylene deflagrations and detonations.

Mr. CUBBAGE replied that the arrester had been designed specifically for town gas–air mixtures and the upper detonation velocity which could be arrested had been stated. The

detonation velocity of acetylene was higher and thus the present design of flame trap was not applicable. Even if the flame trap were sited close to the source of ignition there was still the possibility with acetylene of autodetonation and thus the present design of flame trap should not be used with acetylene.

Mr. PALMER replied that if the speaker was thinking of acetylene decomposition the quenching distance would be rather small, so it would be difficult to get a crimped-ribbon arrester fine enough to be suitable. The decomposition reaction yielded solid carbon which would tend to block the arrester. Arresters were available for acetylene but not of the crimped-ribbon type; hydraulic arresters were often used. The flow was normally from the acetylene cylinder through a pipe having a cup on the top. There was a ball bearing in the cup covered by a layer of water, so that as the gas passed through it raised the ball and bubbled through the water, then went on to the burner. If a flashback occurred the flame would try to force the water backwards and it would push the ball bearing down into the cup and seal the gas inlet. Alternatively, sintered metal flashback arresters could be used.

When acetylene flashed back it was liable to cause a detonation, which was combustion accompanied by a shock wave, and there had been cases where the shock wave had penetrated through the arrester and re-ignited the acetylene on the inlet side. In some circumstances, it was advisable to use two arresters in series.

Dr. W. E. F. NAISMITH said that he was interested to hear Cubbage say that, when a detonation went round a bend, the velocity was reduced and that some run up was thereafter required to achieve the detonation velocity. Was it right to deduce from that, that when detonation was expected, the most suitable site for the flame arrester was just round the bend?

Mr. CUBBAGE replied that when a detonation entered a bend the flame velocity was apparently reduced since there was a time delay in the bend. The actual flame velocity in that region was not known. Furthermore, it was necessary for the flame after leaving the bend to travel through a length, which was very short, of pipe before a stable detonation was re-established. He agreed that it would appear that the best place to put a flame trap would be immediately after a bend so long as it was known that a detonation was coming down the pipeline. In general, however, it was more likely to be deflagration coming down the line, in which case it would be better to put the flame trap before the bend since it has been shown that a deflagration accelerates through a bend.

Dr. G. MUNDAY raised the question of the curve for flame velocities as compared with Reynolds Number. He was glad to see their curves were similar to those he used in his paper and suggested that two different laws might be the matter of configuration as opposed to the matter of size. He asked Rasbash if the upper line was for square ducts or circular.

Dr. RASBASH replied that one duct was circular, 6 in. in diameter, and the other a one foot square duct, so that there was indeed a difference in configuration besides a difference in diameter. There was, however, some justification for his approach from other results, for example, on maximum pressures, for which it had been found that as long as the ratio of length to diameter was the same, there was no difference between circular ducts and the square duct. It was assumed in the paper that this difference in shape did not play a part in the rate of combustion; but it might. He was fully conscious that more precise information was needed before the relation could be fully established. It had been possible to make calculations of rates of combustion and correlate them

with the turbulence factor ahead of the flame, but a more specific investigation was needed to corroborate the calculation. It was important because it was that type of correlation which allowed extrapolation to conditions outside the actual experimental information. The upper line in the correlation was for the circular duct.

Mr. S. D. KEMP said that he was impressed by Wade's complete faith in mechanical seals. What was the maximum shaft size on which he had experience of them?

Mr. WADE replied that mechanical seals had been used on fairly large rotary compressors and had been in use for a long time. Whilst there had been failures, there had been no drastic failures; whilst there had been leaks there had been no large leaks. The shafts on these compressors were 3 to 4 in. diam. A good deal of work had been done on smaller pumps with a great deal of success. Sometimes double seals had had to be used in difficult applications and if the pressure of the flushing medium was kept higher than that in the pump quite difficult liquids were contained successfully. Seals were widely used and he had confidence in them.

Mr. P. L. CHARLESWORTH said that on a plant of the size described by Wade, he imagined that the amount of liquid in the plant at any given time would be considerable. What would the procedure be if there was a fire? Would it be regarded as safer to leave the liquid hydrocarbons inside the vessels or to dispose of them rapidly through the blow-down system? If so, were there facilities for remote operation of blow-down valves?

Mr. WADE replied that some blow-down valves were remotely operated and of course all vessels were fitted with relief devices which vented to the blow-down system. There were procedures for dangerous situations and it depended on what kind of conflagration or upset it was to initiate the kind of protective action. He would, however, hate to think of an olefine plant in which the whole of the inventory had to be blown down by hand.

Dr. C. A. CURTIS said that the thickness of the whole assembly of the flame arrester was given, but what about the gauge of the metal? Perhaps that could be changed so that the flame arrester was made more effective without getting a larger flame arrester.

Mr. PALMER replied that with the crimped-ribbon type it was the cross-section and length of the aperture that really governed the effectiveness of the arrester, rather than the thickness of the crimped metal. All the arresters tested had ribbon of same the thickness, about 0·002 in. A slight variation would not make much difference, but if the ribbon were made a lot thicker it was possible that the performance of the trap would diminish. The resistance to gas flow would of course be increased.

Mr. CUBBAGE said that the amount of heat that had to be taken out of a flame to quench it was relatively small. That had been proved and flame traps had in fact been made of, among other materials, brown paper and pvc tape. They were just as good for arresting flame as the metal ones. The only disadvantage was that the leading edges of the pvc and paper were damaged by the incident pressure wave, and that of course in practice would entail more frequent replacement of the arrester than is necessary with arresters of crimped metals.

Mr. P. GRANTHAM asked which was regarded as the primary mechanism of the flame arrester—termination of the chain reaction on the walls or heat removal?

Mr. PALMER replied that he did not think it was possible at present to decide between possible mechanisms because they both obeyed the same form of transport laws. A heat-transfer mechanism was a satisfactory basis for the interpretation of results. In pre-flame reactions, the nature of the surface of the walls was very important; quite different results could be obtained by changing the surface coating of the walls of a vessel. With flame arresters, the type of wall did not appear to have any effect on flame-quenching ability, even when the wall was coated with effective chain-terminating materials.

The nature of the flame-quenching mechanism was, however, still an open question.

Mr. D. CONNER asked Wade what type of storage he recommended for low pressure gases from the safety point of view. What advantages did floating roof type storage tanks offer over conventional storage?

Mr. WADE explained that floating roof tanks were required because the hydrocarbon liquid had a low flash point, a wide range of flammability, and a low vapour pressure. With higher vapour pressure hydrocarbons the chance of getting a dangerous atmosphere was less because the percentage of air in the atmosphere of the tank would be lower. Clearly, one way of excluding air from the tank atmosphere was to avoid having any gas space in the tank and that was why floating roof tanks had been chosen. Another reason for using floating roof tanks, though not applicable in this case, was to avoid losses through evaporation.

The CHAIRMAN asked why the tanks were not enclosed as well, if a closed system was to be used for the refinery.

Mr. WADE replied that, in the case of his works, some of the storage tanks were by the riverside and the rest of the process was some four to five miles distant. Moreover, the large storage tanks were capable of standing only a few inches of water whilst the normal plant blow-down system was designed to withstand a pressure of 20–30 lb/in² gauge.

Mr. KLAASSEN said he thought Wade's approach to safety was optimistic, while his own might be a bit pessimistic. Wade assumed that mechanical seals would not leak and that leaks could be cured quickly. He himself started by assuming that they did leak.

Mr. WADE replied that he hoped he had not given the wrong impression. He wished to stress that confidence in being able to avoid hazardous concentrations of gas had been increased by looking carefully at the design of equipment and great pains were taken to see that hazards did not arise. It was only where a series of unlikely situations arose that the area became dangerous and it was only these situations which were considered for Class " B " areas—*i.e.* if a very *reliable* equipment was in *the open* it would be called Class " B " and *non-sparking* equipment would then be used.

I.C.I. was normally criticised for being too safety-conscious. He would not like to give the impression that I.C.I.'s attitude had changed. The attitude toward safety was still one where safety had the highest degree of attention paid to it.

References

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