

## DISCUSSION OF PAPERS PRESENTED AT THE SECOND SESSION

Dr. R. N. LACEY asked if Dr. Burgoyne could indicate whether in a cylindrical vessel with the ratio  $L/D$  appreciably greater than 1, it would be preferable to place the explosion relief vent at one end of the vessel at right angles to the longitudinal axis, or to place it nearer the middle of the vessel, parallel to that axis.

Dr. BURGOYNE replied that it was best to have the vent as near the source of ignition as possible. If a particular source of ignition was suspected, he thought that that would be the over-riding consideration. Otherwise, he felt that the question was more relevant to the paper presented during the third session on "Explosion Reliefs for Duct Systems" which related to venting of longer chambers and venting in pipelines.

Mr. P. VENEMA asked Dr. Burgoyne if he would expect to get different results from exploding pentane vapour or mixture in a sphere, and what the effect of the location of the ignition point in a sphere would be.

Dr. BURGOYNE replied that if a mixture in a sphere were ignited at the centre, the flame-front, in principle, reached all points on the vessel wall at the same moment. In those circumstances the pressure rise stopped abruptly and the explosion was complete in the shortest time possible for the volume of mixture concerned. In practice, convective effects upset the symmetry of the system to some extent. On the other hand, if the vessel were not spherical, the explosion flame reached certain parts of the vessel wall before others, with the result that the duration of the combustion was extended and the pressure rise ceased more gradually.

Dr. J. F. PRESTON said that he had understood Dr. Burgoyne to say that the pressure throughout the vessel was fairly uniform during the pressure rise. He wondered how Dr. Burgoyne and his colleagues had identified that experimentally.

Dr. BURGOYNE replied that the point had not been investigated in their experiments, but the pressure was communicated throughout the vessel at pressure wave velocities which were large compared with the rate of progress of the flame front. It was generally agreed that, in a compact vessel where no great distances were involved, the pressure could be taken as being uniform. He and his colleagues had nothing new to say on that subject.

Mr. R. H. B. FOSTER said that Dr. Burgoyne and his colleague had brought out a very important point: that a relief valve was better than a bursting disc as a safety device. He asked whether, in many cases, it would be necessary to employ a bursting disc because the relief valve would be of too great a size for practical purposes.

Dr. BURGOYNE replied that there might be that reason, and other reasons as well, for preferring a bursting disc. In the paper, they were merely pointing out that, other things being equal, one did get rather better performance in some circumstances with the smoothly-operating device. He thought that there was one practical advantage possessed by a hinged flap or spring-loaded valve; it could be made mechanically quite strong to external influences while still being capable of relieving internal explosion readily.

Dr. W. E. F. NAISMITH asked Dr. Bett what explanation he had for the increase in the explosion pressure of ethylene oxide when nitrogen was added. Normally, when nitrogen was added, the explosion pressure was reduced. From Fig. 8 in the paper by Burgoyne, Bett, and Muir, however, the explosion pressure appeared to rise to a maximum at about 60% nitrogen, and then decrease until at about 67% nitrogen the mixture was non-explosible.

Dr. BETT replied that Fig. 8 showed the maximum pressures developed on igniting various mixtures of nitrogen and ethylene oxide in which the partial pressure of the latter was maintained constant at 125 lb/in<sup>2</sup>. Thus the total pressure of the gas mixture before ignition increased as more nitrogen was added to the ethylene oxide and that accounted for the increase in the explosion pressure as the nitrogen content of the mixtures was raised from 0 to 60%. On the other hand, the ratio of the maximum explosion pressure to the total initial pressure decreased from 6.1 to 4.3 over the same range of composition. The reason for that was that an increase in the proportion of nitrogen decreased the amount of ethylene oxide which decomposed. When the nitrogen content exceeded 60% the effect was pronounced and resulted in a marked decrease in the ratio of the maximum explosion pressure to the initial pressure. At the limit, 67% nitrogen, all the ethylene oxide remained undecomposed and the ratio was unity. That served to show that, for any application in which an inert diluent was required to suppress the decomposition of ethylene oxide, it was important to ensure that sufficient diluent was used.

Mr. J. R. BLANCO said that his impression on reading the paper of Hess and Tilton was that they were referring throughout to total pressure in their storage vessels. Referring to Table I in the paper by Burgoyne, Bett, and Muir, if that were the case, it would mean that their initial partial pressure was, in fact, about 18 lb/in<sup>2</sup> gauge. By reference to Fig. 7 of the paper that would correspond to a nitrogen percentage of about 42% volume. He asked for Dr. Bett's comments on that.

He also asked if Dr. Bett ascribed the different effects of the different metallic igniting elements to a catalytic influence.

Dr. BETT replied that Hess and Tilton gave the percentages of various diluents needed to suppress the explosive decom-

position of ethylene oxide at an initial pressure of 30 lb./in<sup>2</sup>g. Unfortunately it was not clear whether the pressure was the partial pressure of the ethylene oxide vapour or the total pressure of the gas mixture ; furthermore, the temperature at which the experiments were carried out was not stated explicitly. In preparing Table II (page 34) he and his co-authors assumed that the pressure referred to the initial pressure of ethylene oxide vapour before the inert diluent was added, and that it corresponded to the vapour pressure of ethylene oxide at about 43° C. If the alternative interpretation were correct, then the pressure of ethylene oxide must have been adjusted for each diluent investigated ; in the case of hydrogen and nitrogen it would have been about 33.5 lb/in<sup>2</sup> while in the case of butane 43.5 lb/in<sup>2</sup>. As Mr. Blanco pointed out, that assumption reduced the difference between the percentage nitrogen needed to suppress the decomposition of ethylene oxide at a partial pressure of 33.5 lb/in<sup>2</sup> found by the authors and that found by Hess and Tilton, to 42%-25% *i.e.* 17%. In the other hand, Hess and Tilton assumed that the partial pressure of ethylene oxide in the range 15 lb/in<sup>2</sup> to 75 lb/in<sup>2</sup> had no effect on the percentage of nitrogen needed to suppress the explosive decomposition; thus, the discrepancy between the two sets of results depended on the pressure at which the comparison was made.

Dr. BURGOYNE said that he thought that the catalytic properties of the igniting elements were not important. Burgoyne, Bett, and Muir had, by their method, communicated more energy to the gas by the source of ignition than had Hess and Tilton. It would be noticed that they had investigated, to some extent, the effectiveness of the source of ignition, and the energy needed to get what seemed to them to be rational results. They had felt that Hess and Tilton did not, in fact, use a sufficiently energetic source, and also, did not use the most favourable type of source. It had been shown, for example, with the explosive decomposition of acetylene that fusing wires were more effective and reliable sources of ignition than just heated wires. The present authors thought their own source of ignition was more reliable and effective than Hess and Tilton's and therefore gave realistic results.

Mr. K. N. PALMER asked the authors whether any consideration had been given to using an explosion inhibitor rather than an inert blanketing material such as nitrogen ; in that case, one might be able to use an amount smaller than the rather large quantities of nitrogen required.

Dr. BURGOYNE said that they had not given any particular consideration to the point. He was not, at the moment, aware of any powerful inhibitor of the decomposition reaction. A mild retardant would be unlikely to have any significant effect upon the flame reaction involved in the explosion.

Mr. P. VENEMA said that perhaps carbon dioxide might act as an inhibitor.

Dr. BURGOYNE said that Hess and Tilton had tried carbon dioxide and had found it was a little, though not much more, effective than nitrogen. That would be expected on the grounds of its greater heat capacity and it did not seem as if any chemical inhibitory effect was involved.

Mr. C. A. CROSS asked about the apparatus used for the ethylene oxide decomposition. He had noticed that the

pressures seemed to rise toward the design limit of the apparatus. He had looked through the paper by Burgoyne, Bett, and Muir, and could not see any provision in the way of relief. How would the apparatus have failed if, by some change, pressure had gone above the design limit; was apparatus standing the middle of a laboratory, or was it properly protected ?

Dr. BETT said that no relief against over-pressure was provided for the explosion vessel. Since the vessel was designed so that the inner layers of the steel vessel would be on the point of yielding under a static pressure of 3000 lb/in<sup>2</sup>, it should have been capable of withstanding a dynamic load of 1500 lb/in<sup>2</sup> without yielding, even if the loading had been instantaneous. In practice it was found that the minimum time taken to develop the explosion pressure was over 1000 times greater than the calculated natural period of vibration of the cylindrical part of the vessel. Under those conditions the loading was virtually static and the bursting pressure of the vessel was predicted to be about 6000 lb/in<sup>2</sup>. Thus the factor of safety, based on the bursting pressure, was estimated to be about 4 at the maximum operating pressure. Since the steel used for the pressure vessel was very ductile and since care was taken in the design to eliminate, as far as possible, all stress raisers, brittle failure was considered unlikely and the vessel was located in a corner of the laboratory without any protection other than that afforded by its electrically heated oven.

If, by some chance, the pressure had continued to rise above 1500 lb/in<sup>2</sup>, the authors consider that failure would have occurred at the semi-confined nickel gasket which formed the joint between the head and the body of the vessel. If, in the absence of any leakage at the mechanical joints, the pressure had continued to rise, the body of the vessel would have deformed considerably and then burst. The mode of failure in this case would probably have taken the form of a longitudinal crack.

Dr. D. J. LEWIS asked if Dr. Burgoyne's conclusion about a relief valve behaving more effectively than a bursting disc would apply to a fast explosion such as one would get from an hydrogen/air mixture.

Dr. WILSON replied that, in general, the allowable opening-time of a relief-valve increased with the dimensions of the vessel and decreased with increase in the burning velocity of the explosive mixture. In their work it was easy to make the opening-time much shorter than the duration of the explosion, but with fast-burning mixtures, particularly in small vessels, it might be difficult to achieve. A bursting disc might then be preferred, especially if the shock of its bursting did not cause a significant increase in the rate of combustion.

Dr. G. R. FULTON referred to a statement that propylene oxide was stable under conditions which caused ethylene oxide to decompose explosively but that under higher temperatures and pressures it may be made to decompose. What evidence was there of that ? Had the authors done any work on it ? What were the limits for propylene oxide ?

Dr. BETT stated that the authors had attempted to decompose propylene oxide vapour at a temperature of 125° C and pressures up to 165 lb/in<sup>2</sup> but they had not observed any decomposition using a fused nichrome wire as the source of ignition.

Dr. BURGOYNE said that propylene oxide was capable of exothermic decomposition, and one believed therefore, that at a sufficiently high pressure and temperature it would be capable of sustaining a decomposition flame ; but they could not make any prediction as to the temperatures and pressures concerned. The authors could only report the negative results of their tests up to 165 lb/in<sup>2</sup> at 125° C.

Mr. D. R. M. FRYER asked if Dr. Derbyshire could say something about the basis used for the design of the blast walls surrounding the equipment.

He was thinking in terms of relating the explosion in the vessel to the effective wall strength and other factors such as vessel design and location.

Dr. DERBYSHIRE said that the design of the blast walls surrounding the equipment was the responsibility of the Division Engineering Department. Research Department either computed or measured the maximum explosion pressures that would be reached in the various plant units in the event of an explosion. Using that basic data Engineering Department then designed the blast walls in conjunction with the explosive experts at Nobel Division.

Mr. V. KENWORTHY said that Dr. Derbyshire relied on the fact that the plant protection against a back blow from the condenser to the autoclaves was insured because the partial water vapour pressure was high when the plant was running. Did that apply when they were starting up and closing down the plant ?

Dr. DERBYSHIRE said that although it was certain that the gaseous contents of the autoclave were non-flammable once normal operating conditions had been reached, it was quite possible that during the start-up of a batch, when the temperature and pressure were uncontrolled, the composition of the gas might pass through the flammable region. At the beginning of a batch the autoclave was pressurised with nitrogen but this would probably be insufficient to keep the gas non-flammable. During the main part of the oxidation and during the pressure let-down at the end of a batch, when the temperature and pressure were controlled, the gas in the autoclave was non-flammable.

Dr. L. COHEN asked if it was possible to say what was the nature of the ignition source one could expect.

Dr. DERBYSHIRE replied that possible ignition sources were numerous. There were many intermediate oxidation products which, in the presence of nitric acid might undergo exothermic decomposition and serve to ignite an explosion. Another possible source was a discharge of static electricity. However, very little work had been done in attempting to define the nature of the ignition source.

Mr. K. M. HILL said that Dr. Derbyshire seemed to have based the safety of the plant on the isolation of the individual items : for example, he had paid particular attention to that approach on the condenser, where he had the bursting discs at either end at the right angle bend. What would Dr. Derbyshire expect to happen in the way of second order effects ? The bursting disc had gone, the very high pressure had been relieved, but quite considerable pressures were travelling around the system which could cause physical mixing of the materials, changes to conditions outside the operating limits

in the original autoclave, and similar effects going right through the baffle tank.

Dr. DERBYSHIRE said that if an explosion occurred in the condenser, then the relative volumes of the condenser and buffer tank were such that the gas coming from the condenser would not significantly alter the composition of the gas in the buffer tank. Did Mr. Hill mean that oxidising gas from the condenser might be passed into the autoclave and so produce an inflammable gas mixture ?

Mr. HILL said that when there was an explosion, there was nothing that he could see to stop the distribution of the contents of the autoclaves throughout the whole system. Pressure and vacuum waves were typical of such an event and it seemed to him that there was not, then, positive isolation.

Dr. DERBYSHIRE said that the pressure control valve effectively isolated the condenser from the buffer tank ; the contents of the autoclave could not be passed to the buffer tank. It was true that there was no positive isolation between condenser and autoclave but in the event of an explosion in the condenser it was improbable that the high pressure gas would get into the autoclave fast enough to pressurise it to any significant extent.

Mr. E. WALLER asked if it was not possible to get a build-up of nitro-compounds in the nitric acid and still form dangerous gases. Because the nitro-compounds were absorbed in the nitric acid and the nitric acid was re-used.

Dr. DERBYSHIRE replied that the nitric acid at the end of a batch was thrown away ; the recovered nitric acid came from the nitrogenous gases evolved during the oxidation. There was, therefore, a purging out of the system and the concentration of nitro-compounds did not build up.

Mr. C. A. CROSS asked what sort of arrangements were made to deal with the rather unpleasant materials that would be discharged if one of the safety devices ruptured, particularly on the condenser, in the event of an explosion in the condenser.

Secondly, on the use of a device to monitor the *p*-xylene content of the gases leaving the condenser, he always felt that continuous sampling devices involved a long time lag and were often somewhat unreliable. Had the possibility been considered of using a gas exit temperature from the condenser as a warning, because it seemed to him that, if action was taken when that temperature rose above the critical level, probably all eventualities would be covered.

Dr. DERBYSHIRE said that the buffer tanks and autoclave and condensing systems were behind very high blast walls. The explosion vents were arranged so that in the event of bursting, the liquid would not be projected over the blast walls. After such an event the enclosure within the blast walls would be washed down with water.

The temperature of the gas leaving the condensing system was in fact measured, but this did not define the *p*-xylene content of the gas since the *p*-xylene could be carried over as a fine mist or spray. The lag involved in continuous sampling had been reduced to negligible proportions.

Dr. C. A. CURTIS said Dr. Derbyshire had mentioned that some nitrogen oxide was absorbed by the nitro-compounds

and the explosive mixture then was soluble in the nitric acid and went to the bottom of the absorber. Was the nitric acid used later on, again in the oxidation process ?

Dr. DERBYSHIRE said that the recovered acid from the absorber was mixed with fresh acid and used again. The amount of nitro-xylenes present in the recovered acid was extremely small.

Mr. E. PENNY asked if Dr. Derbyshire had any trouble with the maintenance of the bursting discs at the end of the condenser.

Dr. DERBYSHIRE said that was a problem but there was a standard bursting disc change after a definite number of batches. It was rare that a disc failed prematurely due to corrosion.

Mr. D. ORMSTON asked if the plant as described in the paper was as it had originally been designed or had it been found necessary in the light of experience to carry out modifications for safety reasons. Had there been, in fact, any explosions on the plant?

Dr. DERBYSHIRE said that quite a few alterations had been made for safety reasons in the light of experience.

His colleague, Dr. GOODINGS, said that no major incidents had occurred on the plant.

Mr. F. REVILL said that, with regard to the chemicals used, it seemed that the plant might be weakened by corrosion and asked if special precautions had been taken on that account.

Dr. DERBYSHIRE said that he could not give an authoritative reply to the question. The plant had been constructed of a certain type of stainless steel with a corrosion allowance and no trouble had been experienced with corrosion.

Dr. R. N. LACY asked if the assumption that the ratio of nitric oxide to nitrous oxide was constant was a valid one, and whether the effect of variation of that ratio on explosion limits had been studied.

Dr. DERBYSHIRE said that the ratio of nitric oxide to nitrous oxide only remained constant if the buffer tanks were being fed from a number of autoclaves. If the gas from only one autoclave were passed to the buffer tanks then the ratio of nitric oxide to nitrous oxide varied considerably. The limits of flammability of *p*-xylene in mixtures of nitrogen oxides did depend very markedly on the ratio of nitric oxide to nitrous oxide but this had been taken into account in defining the safe maximum amount of *p*-xylene in the gas entering the buffer tank.

Dr. S. A. MILLER referred to Dr. Derbyshire's study of a flammability of the hydrocarbon vapours in various mixtures of nitrous and nitric oxides. He asked whether this had confirmed that flammability was markedly greater in nitrous oxide than in nitric oxide.

Dr. DERBYSHIRE replied that it was.

Mr. A. P. OELE asked if it would contribute to the safety of the condensing system if Raschig rings were used as packing for the parts with a big cross-section.

Dr. DERBYSHIRE replied that it would be difficult to do that since the amount of gas evolved during the oxidation was extremely large and that the consequent pressure drop across such a packed condenser would be tremendous.

Mr. D. M. ELLIOTT said that Dr. Derbyshire had intimated that the bursting discs were fitted on the condenser. From papers given earlier in the symposium, it would appear that if the source of ignition were in the reactor, bursting discs ought to be fitted on the reactor.

Dr. DERBYSHIRE replied that bursting discs were fitted to the reactor as well as to the condenser.

Mr. R. J. KINGSLEY said that it seemed a safe assumption that the work reported by Burgoyne, Bett, and Muir had been initiated to get more data on the safe use of ethylene oxide under reaction conditions. He imagined that the work presented would cause some of them to think again about plants they were designing or had designed. Did Dr. Burgoyne think that a review was also required of the conditions under which ethylene oxide was stored? He thought that the conditions deduced from the earlier work were that 35 mole % nitrogen was a satisfactory concentration and he believed that some people now worked with concentrations right up to that value. The work presented did not, perhaps, cover storage conditions but it might be possible to make some prediction. Storage temperatures might be as high as 30° C, with an ethylene oxide pressure of 30 lb/in<sup>2</sup> abs.

Dr. BURGOYNE said that their results indicated that with ethylene oxide at 30 lb/in<sup>2</sup> abs, a nitrogen content of 43% was needed to suppress explosibility. A total pressure of some 53 lb/in<sup>2</sup> abs under nitrogen blanket would therefore be necessary to confer safety in those circumstances.

Dr. F. SJENITZER asked Dr. Burgoyne if he agreed that, in the case of detonation, a bursting disc might be preferable to an explosion valve because of its smaller inertia?

Dr. BURGOYNE agreed with that. The point he had made about the distinction between bursting discs and loaded flaps or valves clearly did not apply to detonation when one had already, as it were, the maximum conditions of explosion propagation, and there was no influence through instability that could lead to any acceleration of the process.

The difference between bursting discs and flaps or valves would be most noticeable with slow explosions. With detonations, inertia would be a particular disadvantage since quick operation would be essential for success. In most detonations, it would be a question whether either type of relief would operate in time to be of any use.

Dr. S. A. MILLER said that he had understood Dr. Burgoyne to say that he did not think that the basic mechanism of the explosive decomposition of ethylene oxide was a chain reaction. That was rather startling because it was contrary to the teaching Dr. Burgoyne normally gave to his students in post-graduate lectures in saying that explosions were chain

reactions. Would Dr. Burgoyne suggest that, at a given moment of time, every molecule of ethylene oxide proceeded to decompose in such a manner as to produce a molecule of methane and half a molecule of ethylene, or must there not be some radical intermediates which were essentially the basis of a chain reaction mechanism.

Dr. BURGOYNE said he had not meant to state that that was not a chain reaction of any kind. What he had intended to say was that he did not know what the detailed mechanism was. They had been talking about the possibility of selecting an inhibitor that would interrupt the reaction in some way. Without a knowledge of the reaction mechanism this seems impossible. Certainly the reaction could not proceed in the molecular manner that Dr. Miller had mentioned and radical intermediates must surely be involved.

Dr. L. COHEN said that he did not want to get involved in an argument on the value of bursting discs compared with loaded flaps but there were a number of points to be considered in designing a pressure relief system. In particular, there was the advantage of the flap over the bursting disc in preventing secondary explosions which were often more severe than primary explosions, particularly with rich mixtures. That effect was due to air being drawn into the vessel, after the initial explosion, which the closing of a loaded flap could prevent. Could Dr. Burgoyne give some guidance on the subject?

Dr. BURGOYNE said that secondary explosion could be an important factor where one had initial explosion either of a fuel-rich combustible mixture, leaving some combustible products inside the vessel, or an explosion such as the ethylene oxide decomposition explosion, which gave nothing but combustible products. With a venting system which allowed air to be drawn in, fresh explosive mixture could be formed which might or might not be more dangerous than that first exploded. It was true that the loaded flap prevented that, but the effect of the reversal of the pressure difference across the flap had to be considered. Would the vessel stand the pressure reversal without collapse?

Mr. Z. W. ROGOWSKI thought that he might throw some light on the maximum pressures obtained with bursting discs and covered vents. He had exploded propane-air mixture in a duct. It was closed near the ignition source and there was a vent on the top of the duct near the end remote from the ignition source. Pressure records obtained with the open vents and vents covered by loosely laid covers showed three peaks. The first was thought to be caused by the inertia of the unburnt gas, the second by the inertia of the vent closure or the inertia of the air outside the duct, and the third by some disturbance to the flame when it was near the vent. With a heavier cover the second peak determined the maximum pressure. With the open vent the maximum pressure was determined by the third peak, which occurred when the flame front was near the vent. When bursting discs were used in smaller ducts, they burst at higher pressures and the maximum pressure was always determined by the maximum bursting pressure of the disc.

Mr. R. J. KINGSLEY asked whether the bursting of a bursting disc could act as a source of ignition. Generally, the conditions downstream of a bursting disc were much more unsafe than those upstream, so that if the disc ruptured for

reasons of over-pressure or because of an internal explosion of a rich mixture, the composition downstream of the bursting disc would invariably be explosive. Could the bursting of the disc supply the energy for a secondary explosion?

Dr. BURGOYNE replied that it could; there had been experiments at the Safety in Mines Research Establishment on that point, which showed that the sudden release either of an explosive mixture or of an inflammable gas into air, or of air into an explosive mixture, could all produce ignition. That was primarily due to shock wave effects but there were always suspicions about mechanical effects being involved in connection with the sudden bursting of the disc. Such ignitions occurred in connection with pressures of the order of 1000 rather than 100 lb/in<sup>2</sup>. For instance, a sudden release of pure hydrogen into the air had been shown to be liable to result in self-ignition from pressures above 70 to 80 atm.

Mr. E. PENNY said, on the matter of ignition following the operation of a bursting disc, that they had had one unfortunate experience with acetylene-oxygen mixture in a storage vessel used in experimental work, when a bursting disc, which had never been replaced, failed from sheer old age. Although the vessel had been installed in a safe place, the issuing gas ignited and a man had been burned. When the vessel was cut open, it was found to contain a very thin layer of dry powdered rust, and they had the idea that the ejection of this rust with the escaping gas, perhaps impacting on the edges of the aperture, had something to do with the cause of ignition.

The moral was that bursting discs should be maintained and replaced regularly. Another moral was that where there was a bursting disc, one should make sure it was doing a job of work. In the particular vessel, the bursting disc had served no useful purpose. Had there been an explosion in the vessel, the bursting disc could not have relieved it. Therefore, in all plant design, it was very important to try and foresee the consequences of failure of the disc and not simply regard it as a cure-all.

Another trouble they had experienced from time to time was when the engineers set the bursting disc too close to the normal operating pressure. Then they always seemed to be in trouble. Unless the discs were replaced after every second or third run they became tired and ruptured prematurely, and a great deal of time was lost and unnecessary work caused.

They always felt there should be quite a reasonable range between the working pressure, the relief pressure, and the yield pressure. He did not think that bursting discs helped very much in reducing the design strength of normal equipment below the maximum pressures which could arise by explosive decomposition of the contents.

Mr. J. I. KRZYMUSKI said that Dr. Derbyshire had described the precautions taken in the design stage to eliminate hazards. No matter how careful the design, there was an inherent danger to the plant, particularly in the start-up period. Mr. Krzymuski wanted to know what was the philosophy which must apply when an accident happened; what happened then? For instance, when the bursting disc on the condenser burst, with the release of toxic vapours, there was a danger of fire near that place: how could fire fighting proceed when there was lighted acid in the vicinity?

Dr. DERBYSHIRE replied that all the necessary safety precautions were in force, respirators were available, and foam

for fire fighting could be piped to each autoclave and condenser bay. He was not in a position to say more on the subject as he was only on the fringe of this particular aspect of the hazard.

Mr. J. R. BLANCO wrote :

Dr. Burgoyne has stated with reference to Table I of the paper by Burgoyne, Bett, and Muir that their results differed from Hess and Tilton's mainly on account of the different ignition sources used. The rate of energy release from the fusion of a Nichrome wire would be considerably greater than that from the heated platinum coil of Hess and Tilton's work. When considering the practical conditions for the safety of storage tanks for liquid ethylene oxide, pressurised with nitrogen, the risk of an internal ignition source arising with energy equivalent to a fusing wire is negligible. Thus there appears to be little reason to depart from Hess and Tilton's recommendations which have been the accepted basis for storage tank conditions.

If there were a severe fire outside the storage tanks liquid ethylene oxide would vaporise and rapidly drive off all the nitrogen diluent through the relief valves. The vapour space would then contain pure ethylene oxide which would inevitably explode when any part of the tank surface became sufficiently hot.

In ethylene oxide reaction systems the danger of ignition by a high energy source may be greater, depending on the reaction conditions and the plant design. However, all the accidental explosions of ethylene oxide vessels which have been described, appear to have been caused by rapid polymerisation due to the catalytic effect of contaminants in the liquid phase. Do the

authors of this paper know of any causes where plant explosions could be attributed to thermal decomposition of ethylene oxide vapour?

Messrs. BURGOYNE, BETT, and MUIR wrote in reply :

The ability of a gas to sustain an explosion flame does not in fact depend on the source of ignition, although of course a particular ignition source may be inadequate to initiate flame in a gas that is capable of sustaining it. We endeavoured in our work to avoid this latter limitation by a preliminary investigation of the adequacy of the source of ignition employed (see Fig. 4, page 32). We fear that Hess and Tilton's sources may not in every case have been adequate in this sense.

Mr. Blanco may be correct in asserting that in storage tanks the risk of an internal ignition source arising with energy equivalent to a fusing wire is negligible. On principle however, we do not think that it is wise to depend for safety upon the absence of all sources of ignition or even any particular kind of source.

So far as storage tanks are concerned, however, practical conclusions drawn from our work may not differ greatly from those arising from the work of Hess and Tilton. Thus, with tanks pressurised with nitrogen to 50 lb/in<sup>2</sup> abs (as is common practice), our results indicate that explosive conditions do not exist in the gas space so long as the liquid ethylene oxide temperature does not exceed about 29° C. This condition may not be difficult to fulfil.

We are glad to say that we have no first-hand knowledge of ethylene oxide reactor explosions from any cause and we do not know with what certainty it has been possible to ascertain the cause of those occasional explosions that have occurred elsewhere.