

# AN EMERGENCY CONDENSING SYSTEM FOR A LARGE PROPYLENE OXIDE POLYMERISATION REACTOR

By M. KNEALE, B.Sc., C.Eng., M.I.Chem.E.,\* and G. M. FORSTER, B.Sc., C.Eng., A.M.I.Chem.E.\*

## SYNOPSIS

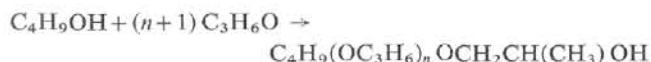
An emergency condenser is provided to control the highly exothermic batch reactions between polyhydric alcohols and propylene oxide in the event of an adiabatic "runaway" reaction due to failure of the primary cooling system. The design and prediction of performance of this condenser is complicated by the process variables which change throughout the batch history.

Vapour-liquid equilibria and kinetics derived from plant data were used to produce a reaction model and the Arrhenius equation to calculate reaction conditions at elevated temperatures during runaway reactions. The heat removal capacity of the emergency condenser is compared with the heat release rates of the reaction and operating procedures are derived in relation to the time interval available for bringing a runaway batch under control.

## The Process

### Introduction

The production of polymers from propylene oxide started during the last war, has reached about  $\frac{1}{2}$  million tons in the world today, and is still rising rapidly. The earliest products were "UCON" lubricants made by the Union Carbide Corporation, the simplest of which were made by step-wise condensation of propylene oxide with butanol:<sup>1,2</sup>



Multi-stage batch reactions were used to make polymers of varying molecular weight, having good lubricating properties, and high viscosity indices. Related products are now used in the lubrication of modern jet engines. Water-soluble lubricants and hydraulic transmission fluids were made in a similar way by random copolymerisation, ethylene oxide replacing 10-75% of the propylene oxide.

Surfactant chemicals developed by Wyandotte Chemicals Corporation in 1950 and marketed under the name of "Pluronics" and "Tetronics" are essentially block copolymers of propylene oxide and ethylene oxide and have found wide use as de-emulsifiers, low foaming detergents and draining aids.<sup>3,4</sup> The Pluronics are frequently obtained from propylene glycol while the Tetronics are based on ethylene diamine.

The polyurethane industry has, however, been the major consumer of polyethers.<sup>5</sup> Paints, varnishes, solid rubbers, flexible foams for cars and mattresses, semi-rigid foams, and rigid foams have required a wide variety of hydroxy-terminated polyethers together with the associated *iso*-cyanates, catalysts, surfactants, and flame-retardants. In the main the polyethers for this purpose are made by condensing propylene oxide with a variety of polyhydroxy-containing initiators; diols such as ethylene glycol and triols such as glycerol and trimethylol propane are used to make polyethers for flexible foams. The polyethers will often have molecular weights of about 2000 to 5000 involving the condensation of the base with up to 80 moles of propylene oxide.

\* Lankro Chemicals Limited, Eccles, Manchester.

Intermediates for rigid foams have lower molecular weights and are obtained by reacting pentaerythritol, sorbitol, and sucrose with approximately two moles of propylene oxide for each hydroxy group present in the base.

Other urethane intermediates are obtained by reacting ammonia and other amines with propylene oxide while fire-retardant materials are produced by the reaction of various phosphorous containing products with alkylene oxides.<sup>6,7</sup>

Although continuous processes have been described for the polymerisation of alkylene oxides, nearly all commercial polyethers are still made in batch processes similar to those used for glycol and non-ionic detergents.

Reaction temperatures between 80°C and 160°C and pressures between 15 lbf/in<sup>2</sup> gauge and 200 lbf/in<sup>2</sup> gauge are used. Modern polyether batch reactors have capacities of 10 to 30 tons.

Although hydrogen ion catalysts and boron trifluorides have been used<sup>8,9</sup> the reactions are mostly commonly catalysed by negative ion catalysts such as amines, carbonates, and alkali metal hydroxides, the initial reaction being the attack of a negative ion on the alkylene oxide.<sup>10,11</sup> The kinetics and polymer distribution equations have been widely studied<sup>12,13</sup> and it has been shown that reaction rate is proportional to the amount of catalyst present and oxide concentration.

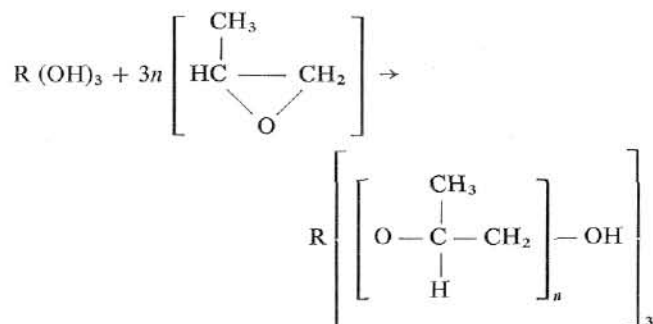
Copolymerisation of ethylene oxide and propylene oxide leads to still different reaction conditions. Whereas propylene oxide produces mainly secondary alcohols under conditions of alkaline polymerisation, ethylene oxide can only produce primary alcohols. Thus there is a competition between the faster reacting ethylene oxide and propylene oxide and the overall speed of reaction is reflected by the ratio of the two oxides present and the means and conditions under which they are introduced into the reaction zone.

It will be realised that the large variety of products, reaction conditions, physical properties, and catalysts give rise to an equally large variety of process conditions.

### Process description

For simplicity, let us consider the manufacture of a homo-

polymer of propylene oxide of molecular weight 3000 starting from a low molecular weight triol:



The final product often contains more than 90% propylene oxide and the reaction can therefore be treated as a polymerisation of that material. The reaction is highly exothermic producing about 714 Btu/lb of oxide reacted.

A batchwise process is used as the reaction rate under acceptable process conditions is low, requiring a high residence time and because of the large number of different products resulting in frequent product changes.

A representation of the equipment is given in Fig. 1.

The heat of reaction is extracted from an external pumped circuit as it is virtually impossible to put sufficient transfer area into a reactor larger than pilot-plant scale.

The reactor is charged with the catalysed starting material, which will only occupy a very small proportion of the final batch volume. Oxide is then continuously fed into the reactor until the batch is made and the reactor is full. Very careful control of reaction temperature, pressure and heat removal rates is necessary to ensure that catastrophic "runaway" polymerisations do not occur.

#### Reaction strategy

Maximum utilisation of the expensive reactor and heat-removal system dictates that the reaction should be completed in the shortest possible time, *i.e.* at the highest possible rate. The major factors affecting the rate are:

- (1). Reaction temperature.
  - (2). Catalyst concentration.
  - (3). Liquid phase oxide concentration (which is synonymous with reaction pressure as the product is non-volatile).
- The limits of reaction temperature and catalyst concentra-

tion are set by such chemical considerations as thermal degradation and purification difficulties.

For the purpose of this paper a reaction temperature of 115°C and maximum pressure of 70 lbf/in<sup>2</sup> gauge have been used.

The reaction strategy is therefore to maximise the pressure (or concentration) for as much of the batch as possible. Two limitations are that:

- (a) the mechanical strength, *i.e.* pressure suitability of the reactor system and
- (b) the possible heat transfer rate of the heat removal system

must not be exceeded. Both these limits are set by engineering decisions based on economics.

The resulting batch history is one during which nearly every variable, including the following, changes with time:

- Polymer (product) weight.
- Polymer molecular weight.
- Batch volume.
- Catalyst concentration.
- Reactant (oxide) concentration.
- Reaction rate (*i.e.* lb/h of oxide reacted)
  - (*i.e.* Heat production rate)
  - (*i.e.* Heat removal rate).
- Oxide feed rate.
- Reactor pressure,

while the following parameters are kept constant:

- Number of moles of polymer.
- Batch temperature.

The desire to maximise reactant concentration or pressure leads to a batch history which falls into three distinct stages:

- (1). *A pressure build-up stage* during which the oxide feed
  - (i) reacts, and
  - (ii) builds up the concentration corresponding to the desired level.
- (2). *A controlled pressure stage* during which the oxide feed
  - (i) reacts, and
  - (ii) maintains the concentration required by the ever increasing batch size.
- (3). *A reacting down stage* at the end of oxide addition during which the residual concentration is allowed to react away.

This is illustrated in Fig. 2.

The problem is complicated by the fact that the vapour/liquid equilibrium is a function of molecular weight so that this relationship is also variable with time.

#### The Safety Problem

With the concentration of unreacted oxide reaching nearly 30% and ever-increasing batch sizes we are now in the position that we have a catalysed polymerisation proceeding in the presence of many tons of unreacted material. That such systems can be adequately controlled has been demonstrated in our plants daily for nearly eight years. We have also occasionally demonstrated that well-designed control systems fail and have then observed with some apprehension the extremely rapid exponential runaway temperature rise that results.

A constant-temperature exothermic reaction implies that at all times the heat of reaction is exactly removed. Generously designed heat transfer equipment (including the whole range of heat exchangers, process pumps, water lines

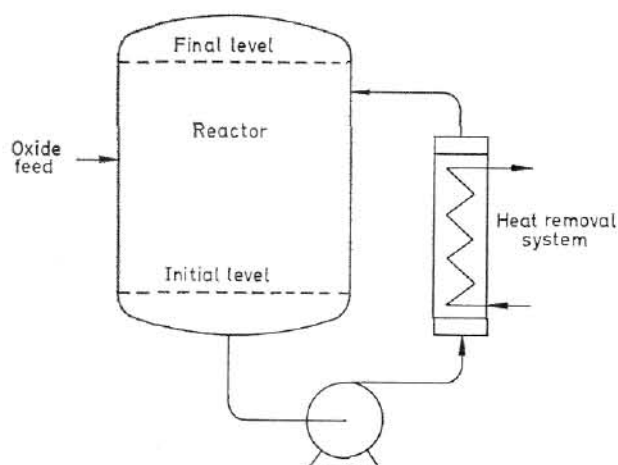


Fig. 1.—Reaction scheme for the batchwise polymerisation of propylene oxide

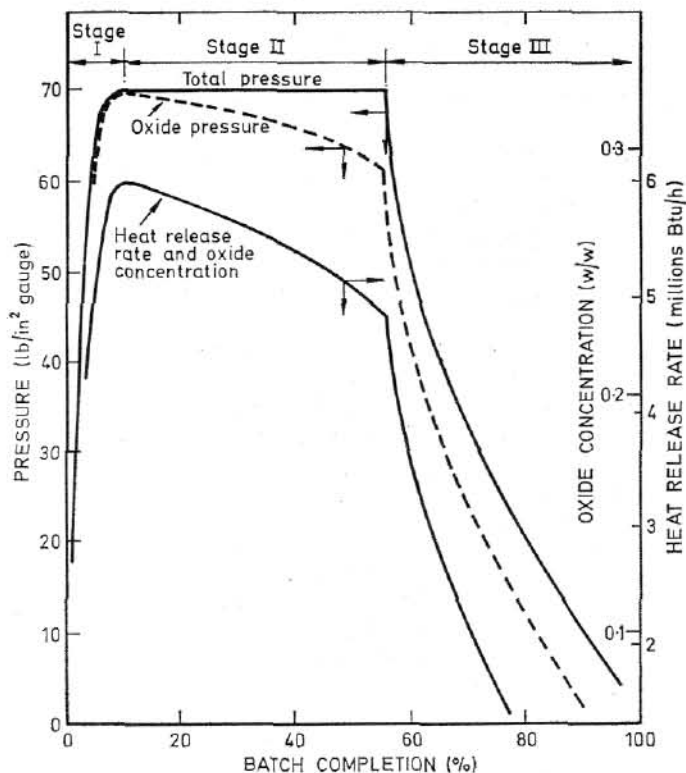


Fig. 2.—Heat release, concentration of oxide, oxide pressure, and total pressure plotted against degree of batch completion

pumps, and cooling towers), together with carefully designed automatic instrumentation, most of it duplicated, ought to preclude the possibility of a runaway reaction. There are, however, a number of conditions, in themselves unlikely, which cannot be designed away at reasonable cost and which may, if combined with failure of instruments or standby equipment, lead to the start of an uncontrolled reaction. Examples include:

The simultaneous failure of normal and standby mechanical equipment, leading to loss of cooling capacity.

The simultaneous failure of normal, standby, and alarm instruments leading to excessive concentrations and heat release rates.

Operator error, for example, in the preparation or measurement of catalyst or inclusion of stray catalytic material.

It was considered essential that the operator should have at his disposal one final and large piece of emergency equipment which would cope with a runaway condition even if noticed some minutes after it commenced.

#### The Emergency Condenser

The condensing temperature for propylene oxide lies between 65°C and 100°C for pressures between 25 and 85 lbf/in<sup>2</sup> gauge and gives a large possible temperature difference against available cooling water. In view of the high condensing coefficient possible a condenser seems an attractive solution for obtaining a large heat flux quickly in order to halt an incipient runaway reaction. Such a condenser was designed on the basis that it should be capable of removing at least twice the maximum operating heat release. Fig. 3. shows such a system.

As the reaction rate doubles for every 10°C rise in temperature the condenser will only be of use for the short period until even its capacity is exceeded. Although the condenser

performance rises with temperature it does so much more slowly than the reaction rate.

The operator therefore has a limited time margin for commissioning the condenser in order to bring a runaway reaction under control. This varies throughout the batch as is shown below.

#### Prediction of Condenser Performance

##### The reaction model

The variables required to predict the performance of the condensing system at every stage during the reaction were calculated from plant derived kinetics and from vapour liquid equilibria measured on the pilot plant.

##### KINETICS

Plant measurements indicate that the kinetics at a given temperature can be well represented by:

$$r = k_1 cS \quad (1)$$

where:  $r$  = the reaction rate (lb mol/h ft<sup>3</sup>).

$c$  = the oxide concentration (lb/lb).

$S$  = the catalyst concentration

$$= S_0/V \text{ (mol/ft}^3\text{)}.$$

As the weight of catalyst is constant, the concentration is reduced as the batch volume increases, so that the total batch reaction rate,  $R$ , is given by:

$$R = Vr = k_1 cS_0 \text{ (lb mol/h)}.$$

Hence:

$$R = kc \quad (2)$$

where  $k = k_1 S_0$ .

It is not claimed that equation (2) is a fundamental expression of the kinetics which are known to be complex but it does represent plant data within  $\pm 5\%$  for all but the very low concentrations ( $c > 0.05$ ).

##### VAPOUR/LIQUID EQUILIBRIA

Vapour-pressure data for propylene oxide in equilibrium with polymers of various molecular weights were measured on our pilot plant at temperatures up to 130°C. Typical

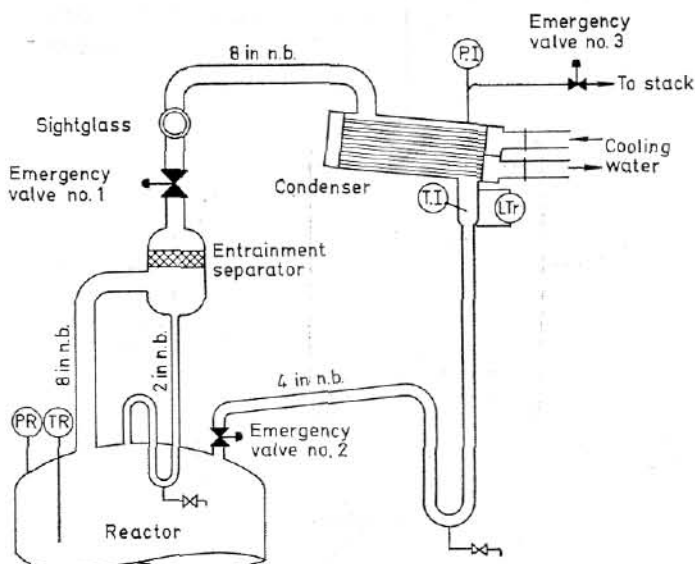


Fig. 3.—Emergency condenser for the propylene oxide polymerisation reaction

TABLE I.—Vapour-pressure Data for Propylene Oxide in Equilibrium with Polymers of Varying Molecular Weight

Molecular weight	Propylene oxide concentrations (w/w) at pressures of:		
	40 lbf/in <sup>2</sup> gauge	60 lbf/in <sup>2</sup> gauge	80 lbf/in <sup>2</sup> gauge
1000	0.160	0.240	0.330
2000	0.150	0.226	0.306
3000	0.143	0.212	0.288

values for oxide concentration versus pressure measurement at 115°C are given in Table I.

These results can be linearised in the concentration range  $c = 0.05$  to  $0.30$  with a maximum error of  $\pm 5\%$  by the equation:

$$p = (237 + 0.021M)c - 3 \quad (3)$$

where:  $p$  = pressure (lbf/in<sup>2</sup> gauge).

$M$  = molecular weight of polymer.

$c$  = concentration of oxide (lb/lb).

The above results apply to uncatylsed mixtures but it has also been demonstrated by measurements of concentration in catalysed reaction mixtures that the effect of the usual levels of catalyst on the vapour liquid equilibrium is very small (which also implies that mass transfer is not limiting). Values obtained for uncatylsed polyethers will give the maximum concentration of oxide in the liquid phase and this was therefore used to obtain a somewhat conservative assessment of the safety situation.

#### STAGE I—PRESSURE BUILD-UP

During the stage of pressure build-up the oxide concentration is built up at maximum rate (governed by the feed pump).

Let:  $N$  = number of pound moles charged to reactor initially.

$b$  = weight of initial charge to the reactor (lb).

$z$  = total weight of oxide added to time  $t$  (lb).

$x$  = amount of reacted oxide at time  $t$  (lb).

$u = z - x$

= amount of unreacted oxide at time  $t$  (lb).

$m$  = total batch weight

=  $b + z$  (lb).

For a constant feed rate:

$$\frac{dz}{dt} = a$$

$$\text{or: } z = at \quad (4)$$

The rate of reaction  $R = kc$  (see equation (2)) or:

$$R = \frac{dx}{dt} = \frac{ku}{m} = \frac{k(z-x)}{(z+b)} \quad (5)$$

Solving equations (4) and (5):

$$\frac{dx}{dt} = \frac{k(at-x)}{(at+b)}$$

$$\text{or: } \frac{dx}{dt} + \frac{kx}{at+b} = \frac{k at}{at+b} \quad (6)$$

This can be solved by integrating by parts to give:

$$x = at - \frac{m}{g} + \frac{b^g}{gm^{g-1}} \quad (7)$$

$$\text{where: } g = 1 + \frac{k}{a}$$

Substituting back into equation (5) yields:

$$\frac{dx}{dt} = \frac{k}{g} [1 - (b/m)^g] \quad (8)$$

And as  $m = at + b$ , this gives the reaction rate as a function of time.

#### STAGE II—REACTION UNDER CONSTANT PRESSURE CONTROL

At a constant pressure of 70 lbf/in<sup>2</sup> gauge we have from equation (3) that:

$$70 = (237 + 0.021M)c - 3$$

The molecular weight,  $M$ , is given by:

$$M = \frac{b+x}{N}$$

And the concentration is given by:

$$c = \frac{z-x}{z+b}$$

The vapour liquid equilibrium equation (3) at the constant pressure of 70 lbf/in<sup>2</sup> gives:

$$70 = \left(237 + 0.021 \frac{b+x}{N}\right) \left(\frac{z-x}{z+b}\right) - 3$$

This can be combined with the rate equation:

$$\frac{dx}{dt} = k \frac{(z-x)}{(z+b)}$$

to give a time relationship:

$$t = D_0 + D_1 x + D_2 x^2$$

$D_0$ ,  $D_1$ , and  $D_2$  are constants.

Unfortunately the system is further complicated by the presence of dissolved inert gases in the oxide feed stream. As the total pressure on the system is kept constant this reduces the partial pressure of oxide particularly as the gas volume over the reactor is compressed. It was therefore found easier to solve the above equations numerically and to allow for the effect of compressing inert gases at the same time.

#### STAGE III—REACTING DOWN

After the charging of oxide has been completed the reaction continues at a decreasing rate due to the decay of residual oxide concentration in the batch:

$$\frac{dx}{dt} = kc = k \frac{(z-x)}{(z+b)}$$

where  $z$  is now the final charge.

$$\text{Hence: } t = D_3 - D_4 \log(z-x) \quad (10)$$

where  $D_3$  and  $D_4$  are constants.

The results are given in Fig. 2.

#### Reactor conditions during "runaway"

##### INTRODUCTION

In the event of primary cooling failure (having stopped the oxide feed) the temperature, pressure and reaction rate will increase at an accelerating rate. In theory the combination of the Arrhenius equation and an overall heat balance should give a temperature/time prediction but it was not possible to solve the resultant equation analytically. The following numerical method was used.

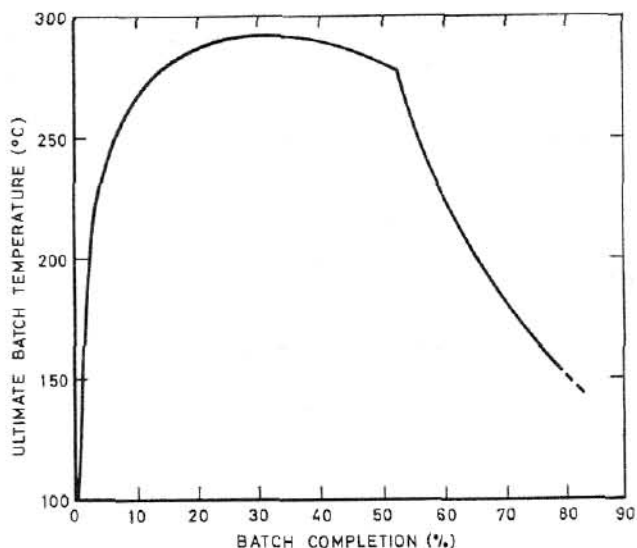


Fig. 4.—Ultimate batch temperature for an adiabatic reaction as a function of the degree of batch completion

#### REACTION RATE AS A FUNCTION OF TEMPERATURE

The increase of reaction rate with temperature was predicted from the Arrhenius equation:

$$k_1 = A'e^{-E/RT} \quad (11)$$

The molal energy of activation used was  $E = 21$  kcal/mol (compared with values of 17–21 reported for alkylene oxide reactions by Weibull and Lowe)<sup>7</sup>.

Multiplying factors,  $F$ , relative to the reaction rate at normal temperature were calculated.

#### TEMPERATURE, PRESSURE AND REACTION RATE AS A FUNCTION OF TIME DURING ADIABATIC "RUNAWAY" REACTIONS

The ultimate temperature possible due to an adiabatic runaway is given in Fig. 4 which assume complete reaction of the unreacted oxide. Temperature rises of nearly 200°C will occur except at the beginning and end of the reaction. It should be noted that the ultimate temperatures will in no case exceed the published value of the auto-ignition temperature of propylene oxide (550°C in air at one atmosphere).<sup>14</sup>

As all variables change rapidly during the temperature rise,

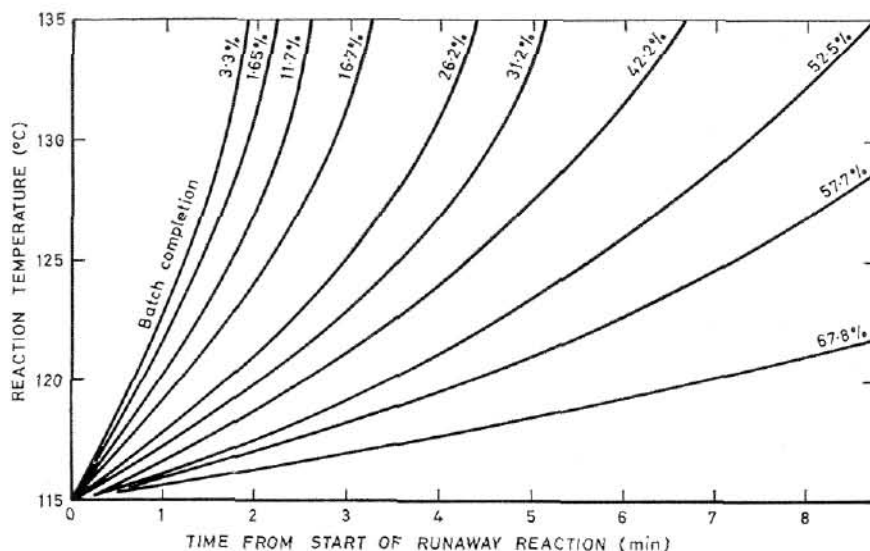


Fig. 5.—Reaction temperature as a function of time from the start of a runaway reaction

temperature rises of 2 degC were taken and the time for these calculated from a heat balance using the  $F$  factors.

The heat balance is:

$$\frac{\Delta Q}{\Delta t} = \frac{H\Delta x}{\Delta t} = HkF \frac{(z-x-\Delta x/2)}{m} = \frac{w\Delta\theta}{\Delta t}$$

Where:  $H$  = the heat of reaction.

$\theta$  = the temperature rise.

$w$  = the water equivalent of the reactants and reaction system. (NOTE:  $w$  varies as the batch proceeds.)

Thus histories relating temperature to time at various stages during the batch were calculated and are presented in Fig. 5.

It will be seen that the highest rate of temperature rise occurs shortly after the start of the batch. This time corresponds to a low mass with an already high oxide concentration and reaction rate. A similar family of curves is derived for heat of reaction versus time from cooling failure (see Fig. 6).

As the temperature rises the pressure increases although the oxide concentration falls due to reaction. It is also necessary to calculate the pressure time curves as these affect the condenser performance.

The vapour pressure equilibrium data can be corrected by a factor:

$$\Delta p = \Delta\theta(5c+0.2) \quad (13)$$

where  $\Delta p$  is the increase of pressure due to a temperature increase  $\Delta\theta$ .

This applies in the range  $\Delta\theta = 0$  to 20°C.

#### Condenser performance

##### TOTAL REFLUX OR TOTAL OFFTAKE

The system devised returns all condensate to the reactor immediately. It can be shown that this total reflux system cools the reactor faster than one in which the condensate is removed. The heat absorbed by the cooling water,  $Q_T$ , is the sum of the desuperheating,  $Q_d$ , and the condensing loads,  $Q_c$ , and unless the condensate is refluxed to the reactor the benefit of the desuperheating load is lost. The danger in removing and storing condensate, possibly containing entrained catalyst, is also avoided. Furthermore, if condensate is removed the reactor and condenser pressure fall more quickly and with it the effectiveness of the condenser. The desuperheating of the oxide vapour from the reactor tem-

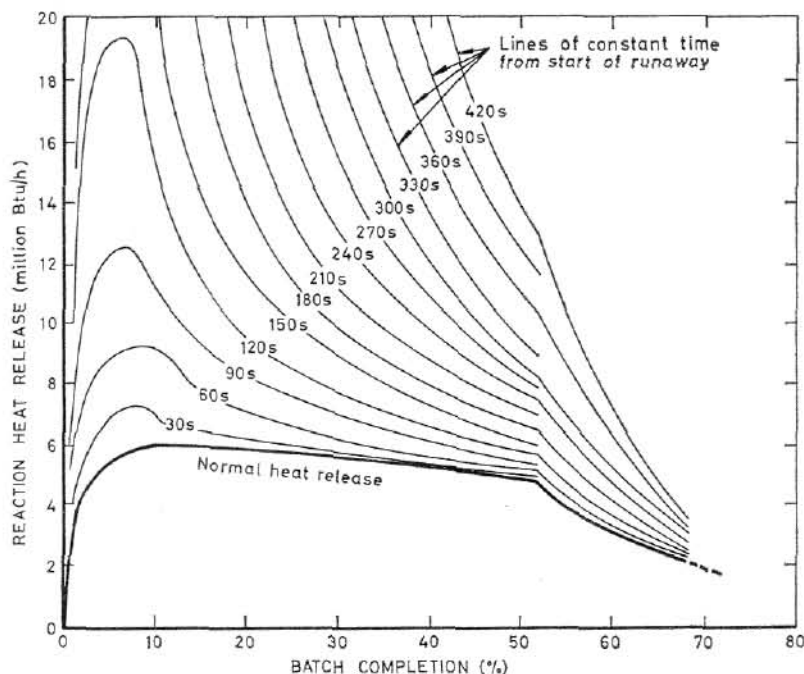


Fig. 6.—Heat release as a function of degree of batch completion during runaway

perature down to its condensing temperature requires a large surface area due to the low heat transfer coefficient. Alternative methods of achieving the desuperheating were considered (*e.g.* vapour/liquid contacting devices) but ruled out for reasons of cost and layout.

#### THEORY

A preliminary calculation based on twice the maximum design heat release rate indicated an area of nearly 2000 ft<sup>2</sup> for the condenser. Such a condenser was designed and its performance subsequently checked by the method here outlined.

It will be shown that the heat removal capacity of the condenser is a function only of the vapour inlet temperature and the condensing temperature (or pressure). Special operating procedures were designed to remove trace inerts which do accumulate during the batch.

The pressure drop due to vapour flow has to be calculated to determine the condensing pressure. This involves trial and error calculations.

At any time from loss of primary cooling, we have determined:

- Reaction temperature,  $\theta_r$ , (°C).
- Reaction pressure,  $p_r$ , (lbf/in<sup>2</sup> gauge).
- Condenser pressure,  $p_c$ , (lbf/in<sup>2</sup> gauge).
- Condensing temperature (from vapour pressure data),  $\theta_c$ , (°C).
- Condenser area,  $A$ , (ft<sup>2</sup>).
- Heat capacity of oxide,  $h$ , (Btu/lb °F).
- Latent heat of vaporisation of oxide,  $L$ , (Btu/lb).
- Cooling water supply temperature,  $\theta_i$ , (°C).

Let the:

- Rate of oxide condensation be  $W$  (lb/h).
- Cooling water outlet temperature be  $\theta_o$  (°C).
- Subscripts denoting desuperheating be  $d$ .
- Subscripts denoting condensing be  $c$ .

$$\text{Thus: } A = A_d + A_c \quad (14)$$

Desuperheating:

$$Q_d = 1.8hW(\theta_r - \theta_c) = 1.8U_d A_d \left[ \frac{\theta_r + \theta_c}{2} - \frac{\theta_o + \theta_i}{2} \right] \quad (15)$$

Condensing:

$$Q_c = LW = 1.8U_c A_c \left[ \theta_c - \frac{\theta_o - \theta_i}{2} \right] \quad (16)$$

From equation (15):

$$A_d = \frac{2hW(\theta_r - \theta_c)}{U_d(\theta_r + \theta_c - \theta_o - \theta_i)} \quad (17)$$

Solving equations (14), (16), and (17) gives:

$$W = \frac{1.8U_c U_d A (2\theta_c - \theta_o - \theta_i)(\theta_r + \theta_c - \theta_o - \theta_i)}{2LU_d(\theta_r + \theta_c - \theta_o - \theta_i) + 3.6hU_c(2\theta_c - \theta_o - \theta_i)(\theta_r - \theta_c)} \quad (18)$$

As  $U_c$ ,  $U_d$ ,  $\theta_c$ , and  $\theta_o$  are all complex functions of the condensation rate,  $W$ , this equation can only be solved by trial and error.

$W$  is calculated for all values of  $\theta_r$  and  $\theta_c$  during the runaway reaction and the total heat removal rate:

$$Q_T = Q_d + Q_c \quad (19)$$

Hence from equations (15) and (16):

$$Q_T = W[1.8h(\theta_r - \theta_c) + L] \quad (20)$$

#### HEAT REMOVAL CAPACITIES

In Fig. 7 the calculated condenser performance is superimposed on Fig. 6 and this enables a comparison to be made with the reaction heat release rates.

Although the whole range of conditions were calculated only the limits of performance are shown by two lines. The lower presents condenser performance at normal operating conditions and it can be seen that the condenser is capable of removing more than twice the heat of reaction for all but the first fraction of oxide addition. In this early period the condensing temperature is low relative to available cooling water but the concentration is such that the ultimate temperature is not excessive.

The upper line shows the ultimate condenser capacity, this being the condition when the condenser performance equals the rate of heat release during a runaway reaction. This is about three times the normal heat release, again except right at the beginning of the batch.

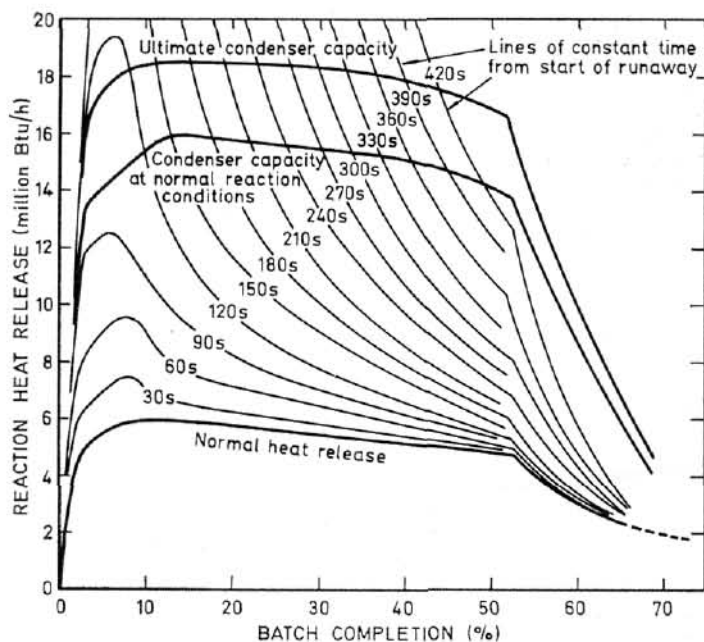


Fig. 7.—Heat removal capacity of condenser and reaction heat release plotted against degree of batch completion during runaway

#### TIME AVAILABLE FOR CONTROLLING A "RUNAWAY" REACTION

The time available for commissioning the condenser in order to hold a runaway reaction is obtained from Fig. 7, being given by the intersection of the ultimate capacity curve with the reaction heat release (constant time) curves.

These times are plotted in Fig. 8. The upper curve gives the theoretically available time assuming the condenser is commissioned immediately the primary cooling system fails. The lower line deducts 40 seconds which is a generous margin for detection and commissioning the system.

It will be seen that in addition to the 40 seconds there is at least one minute after alarm conditions arise before action is essential. This short period rapidly improves as the batch grows.

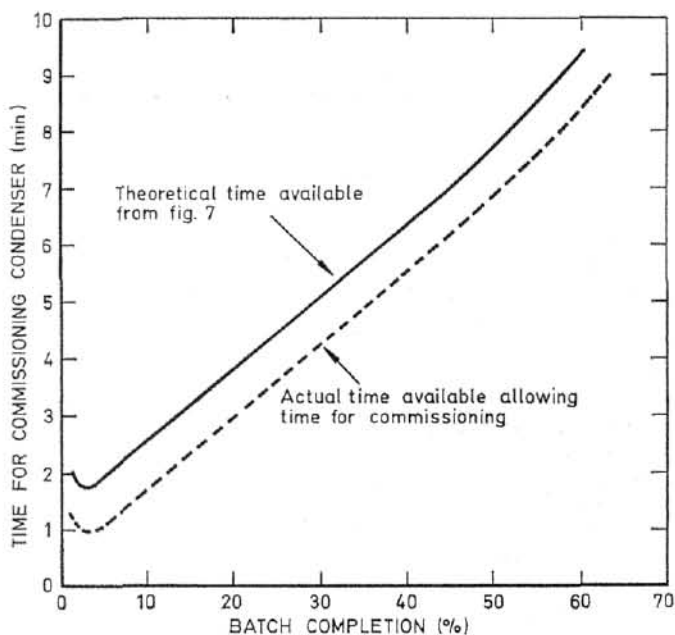


Fig. 8.—Time available for commissioning emergency condenser to control runaway reaction for various degrees of batch completion

#### LIMITATIONS IN PRACTICE

We have discussed in some detail a case where reaction occurs at a high pressure (which is a favourable condition for condensation).

There are many products, particularly co-polymers of ethylene and propylene oxide, where the batch strategy has to be worked out in the light of possible condenser performance.

For reactions or stages involving ethylene oxide only such as occur in the production of block polymers the condenser is virtually useless because of the low condensing temperature. The strategy here will be to limit the concentration of oxide such that a runaway will only raise the temperature to an acceptable level.

For mixed oxide reactions such as occur in the manufacture of random co-polymers the possible condenser performance is reduced and a strategy is adopted to limit the heat of reaction within the condenser capacity.

It is evident that the operating conditions for particular products have to be determined in relation to the safeguards provided by the condensing system.

#### Plant Description and Operation

##### Hardware—(Refer to Fig. 3)

The condenser is of mild steel construction with tubes expanded and welded to fixed tube plates. Condensation occurs in the shell side, which is single pass and sloping to the condensate outlet. Special care has been taken to ensure that there is no hold-up of condensate, *i.e.* that surface area is not wasted in sub-cooling.

Water flows through the condenser at all times. Standby water pumps and an emergency electrical supply are available.

Instruments are provided on the operating level for condenser pressure and condensate temperature and a level alarm is installed at the condensate outlet to indicate possible flooding.

The entrainment separator incorporates a wire mesh demister, is part of the reactor system, and is isolated from the condenser by an electrically actuated 8 in. gate valve (No. 1). The condensate return from the condenser to the reactor is isolated by a similar 3 in. valve (No. 2). A purge

line with 1 in. air operated valve (No. 3) is provided for venting inert gases to stack when first commissioning the condenser. All three valves are operated remotely from the control room and have position indicators and manual overrides.

#### Operation

When an emergency condition arises the operator commissions the condenser in the following way:

- (1). Opens main vapour valve No. 1.
- (2). After 15 seconds opens the reflux return valve No. 3.
- (3). Opens nitrogen purge valve for 10 seconds only and repeats after another 10 seconds.

The condenser is pressurised with nitrogen to 5 lbf/in<sup>2</sup> gauge during reactions. When the main vapour valve is opened the initial pressure differential will produce sonic velocity and the pressure in the condenser will rapidly approach that in the reactor. It has been calculated that this takes only a few seconds and condensation will have commenced before the vapour valve is fully opened, which takes 30 seconds, being limited by the actuator speed. The reflux return valve can therefore be opened before the main valve is fully open. Two purges each of 10 seconds will completely vent the maximum accumulated inerts from the system which would otherwise retard the condensation rate.

It is our experience that operators are reluctant to open reactors under pressure to low pressure condensing systems except in the gentlest possible fashion. This is due to anxiety raised by the high noise intensity associated with sonic flow. The remotely-operated valve actuator has overcome this problem.

It was also feared that the sudden opening to the condenser might cause the mass of the batch to rise bodily under the influence of extremely rapid boiling. However, calculations indicated that at the maximum boiling rate the velocity of the vapour leaving the liquid surface is less than 1 ft/s and although the velocity in the line to the condenser will reach 900 ft/s, that of the gas flowing towards the reactor outlet nowhere exceeds 3 ft/s. These are considered acceptable from entrainment considerations.

#### Operating policies

The operators are encouraged to regard the condensing system as being available for even slight abnormalities: in case of doubt the rule is to use it. The relevant extract from the operating manual is:

"Commission the condenser whenever:

(a) there is any indication of a failure in the primary cooling system

OR (b) there is an excessive heat release rate (i.e. more than 80% of primary cooling capacity)

OR (c) the reaction temperature exceeds the control setting by 2 degC."

An operator is in the control room at all times and duplicated instruments and alarms ensure that any of the above conditions will rouse him.

#### Condenser Performance

The plant was commissioned earlier this year and the condenser performance was tested during pre-start-up checks. A synthetic uncatalysed reaction mixture was prepared and raised to temperature and pressure. The performance was measured by carefully measured cooling rates of many tons of oil and metal.

The results are given in Fig. 9 at various pressure levels and are compared with the predicted performance. This

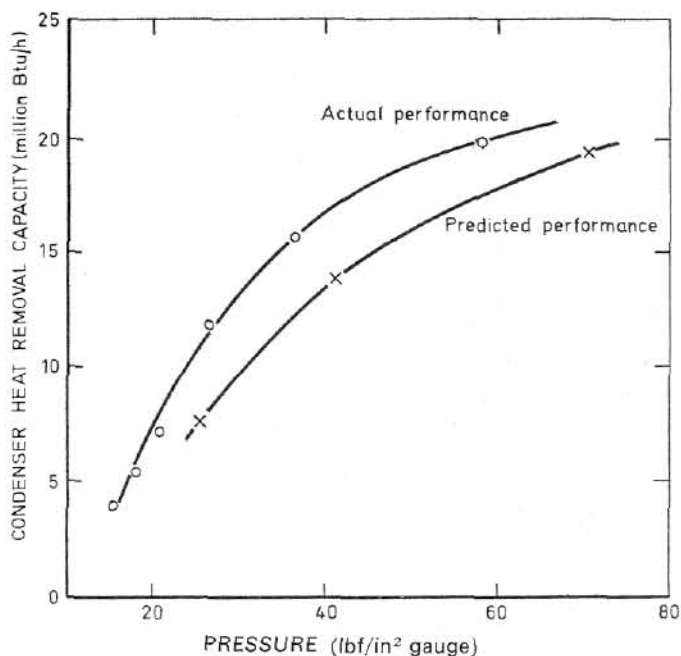


Fig. 9.—Comparison of predicted heat removal performance of the emergency condenser with the calculated performance

predicted performance does not allow for the large fouling factors which were included in the overall heat transfer coefficients in calculating the performance of the condenser as shown in Fig. 7.

The tests were used to educate the operators and incidentally confirmed the importance of purging out the nitrogen.

#### Other Safeguards

The plant has to be safe even if the condenser fails. This failure could arise because of a number of unlikely occurrences (e.g. failure of water, plant, or operator). There are of course many plants which have no such emergency system.

The ultimate protection against over-pressurisation is provided by means of relief valves, bursting discs, and flame traps. In addition the reactors are designed to withstand an internal explosion without rupturing. The venting of large quantities of oxide to atmosphere has been examined in consultation with Dr. J. H. Burgoyne. Whereas we are satisfied that this is safe we prefer to avoid this situation, keep the relief devices closed, and save the material.

#### Conclusions

It has been shown in theory and proven in trials that a condensing system can be designed to cope with large heat fluxes which arise during exothermic "runaway" reactions which can occur during alkylene oxide polymerisations.

It is believed that for reactions involving large quantities of volatile chemicals such a system could find a wider application to improve the safety of plant operation.

#### Acknowledgment

The authors thank the Directors of Lankro Chemicals Limited for permission to present this paper; in particular Mr. R. J. Kingsley and Mr. A. J. Lowe for comments and advice, Dr. R. Dyke for the equilibrium data, and Mr. J. Kelly for much of the computing work.



## Symbols Used

- $A^1$  = proportionality factor in Arrhenius equation.  
 $A$  = heat transfer area of condenser (ft<sup>2</sup>).  
 $a$  = constant oxide feed rate (lb/min).  
 $b$  = weight of initial charge (lb).  
 $c$  = oxide concentration (lb/lb).  
 $E$  = total energy of activation (k cal/mol).  
 $F$  = factor for calculating reaction rate in equation (12).  
 $g$  =  $1 + k/a$  in equation (8).  
 $h$  = heat capacity of oxide (Btu/lb °F).  
 $H$  = heat of reaction (Btu/lb).  
 $k_1$  = specific reaction rate constant (h<sup>-1</sup>).  
 $k$  =  $k_1 S_0$  = overall reaction rate constant in equation (2) (mol/h).  
 $L$  = latent heat of vapourisation (Btu/lb).  
 $m$  =  $b + z$  = total weight of batch (lb).  
 $M$  = molecular weight of polymer.  
 $N$  = number of moles of initial charge.  
 $p$  = pressure (lbf/in<sup>2</sup> gauge).  
 $Q$  = heat quantity (Btu).  
 $r$  = specific reaction rate (mol/h ft<sup>3</sup>).  
 $R$  = overall reaction rate (mol/h).  
 $S$  =  $S_0/V$  = catalyst concentration (mol/ft<sup>3</sup>).  
 $S_0$  = catalyst charge (mol).  
 $t$  = time.  
 $T$  = absolute temperature (°R).  
 $u$  =  $z - x$  = weight of unreacted oxide (lb).  
 $U$  = overall heat transfer coefficient (Btu/h ft<sup>2</sup> °F).  
 $V$  = batch volume (ft<sup>3</sup>).  
 $w$  = water equivalent (lb).  
 $W$  = oxide condenser rate (lb/h).  
 $x$  = weight of reacted oxide (lb).  
 $z$  = weight of oxide charged to reactor (lb).  
 $\theta$  = temperature (°C).

## Subscripts

- $c$  = condensing.  
 $d$  = desuperheating.  
 $i$  = water inlet.  
 $o$  = water outlet.  
 $r$  = reactor.

## References

- Roberts, F. H. and Fife, H. R. *U.S. Patent* 2425 755.
- Toussaint, W. J. and Fife, H. R. *U.S. Patent* 2425 845.
- Vaughn, T. H., Suter, H. R., Lundsted, L. G., and Kramer, M. G. *J. Am. Oil Chem. Soc.*, 1951, **5**, 294.
- Vaughn, T., Jackson, D. R., and Lundsted, L. G. *J. Am. Oil Chem. Soc.*, 1952, **6**, 240.
- Saunders, J. H. and Frisch, K. C. "*Chemistry and Technology*", 1964. (New York: Interscience Publishers Inc.).
- Standard Oil Co. *U.S. Patent* 2 372 244.
- Farbenfabrik Bayer. *German Patent* 918 868.
- Farthing, A. C. *J. chem. Soc.*, 1955, Part IV, p. 3684.
- Rose, J. B. *J. chem. Soc.*, 1956, Part I, p. 542.
- Boyd, D. R. and Marle, E. R. *J. chem. Soc.*, 1914, **105**, 2117.
- Bronsted, J. N. and Kilpatrick, M. *J. Am. chem. Soc.*, 1928, **51**, 428.

<sup>12</sup> Kroch, F. H., Butler, D., and Lowe, A. J. in *Proceedings of XIIIth International Congress on Pure and Applied Chemistry*, Stockholm, 1963.

<sup>13</sup> Weibull, B. and Lowe, A. J. *J. Polymer Sci.*, 1954, **12**, 493.

<sup>14</sup> "*Alkylene Oxides*". (London: Shell Chemicals Ltd).

*The manuscript of this paper was received on 11 April, 1968.*

## DISCUSSION

Mr. T. THOMPSON said that he was at present going through the design and erection of plant very similar to that described, also making use of Burgoyne's specification for containing pressure. It was thought that the main problem would be lack of water. In this case, they were thinking of designing two water-cooling systems, one being a self-enclosed pump system and the water being available from the tower for the other. The main problem seemed to be the cutting off of the water. Was there an emergency supply for the condenser and would there be an emergency supply for the reactor heat exchanger in the system described?

Mr. FORSTER said that it was true that water supply was a prime concern. In their particular case there was a single water supply to the primary heat exchange system which was a liquid-liquid system. There were stand-by pumps. There was stand-by alternator generation of electricity in the event of mains failure. A constant water supply to the condensing system had been ensured but this arranged in series with the liquid-liquid system, and the benefit was gained of having a condenser available to take out heat as well as the primary system.

Mr. THOMPSON pointed out that if it was the same water supply to both and there was a trip-out of the pump due to electrical fluctuations, from that moment the reaction took off and there was no water to the condenser and no water on the reactor heat exchanger which, he would have thought, was the primary runaway condition.

Mr. FORSTER replied that there were five such water pumps in parallel. If it was a case of all five tripping out at the same time, it would be serious but there was a time interval for starting the pump generator which was quite short—about 30 s—at which point it would be possible to put on the water supplying the condenser and cooling system. That was still within the time available for commissioning the condenser, in that the runaway reaction would not start immediately.

Mr. P. WOOLMAN said that he noticed that there did not appear to be a nitrogen blanket on the top of the reaction. He would be interested to know the reason. He understood that ethylene oxide decomposed explosively; perhaps propylene oxide did not do the same thing.

Secondly, when a bursting disc was used, why was the vessel designed to withstand an explosion? He thought that a bursting disc was designed to protect the vessel so that it could be designed for normal working pressure. Surely with the bursting disc bursting and vapour going into the air on top of the bursting disc, an explosive region would be formed which would travel down the vent pipe. Was nitrogen put in to counter this and was nitrogen allowed to enter the vessel when the bursting disc had gone? What happened on an instrument air failure?

Mr. KNEALE said that a nitrogen blanket was not used for reasons which involved a complicated argument and he suggested that Mr. Woolman might like to consult others about it. The principle of designing a reactor to contain an internal explosion followed from a safety criterion which they had tried to adopt: that it could not be supposed that there would never be an internal source of ignition in a reactor. One might say that if the bursting disc was the main safeguard and the plant was perfectly designed the policy need not be adopted but perhaps that was rather a case of belt and braces. A paper given during another session made him think that all the bursting discs had to be re-examined to see if they were as safe as the manufacturers said. Discs were notoriously sensitive to temperature variation and were only regarded as the ultimate safeguard for the operators.

There were facilities for bleeding nitrogen into the stack but that was not done as a normal procedure. One of the things that was reassuring in this respect was that even the ultimate temperatures reached, getting on towards 300°C, were still below the auto-ignition temperature of the materials.

Mr. WOOLMAN asked if the system was designed to fail safe on instrument air or was it normal to have bursting discs as the final safety feature and accept that if an instrument air

failure occurred, the normal protective system would not operate.

Mr. KNEALE replied that the control valves on the emergency condensing system were electrically operated with the provision of an emergency electrical supply; therefore this question was not really relevant to this particular plant.

Mr. FORSTER said that in the event of instrument air failure, the pump would automatically call for cooling. Secondly, the condensing system was not dependent on an air supply anyway. The valves were electrically activated.

Mr. H. FISCHHOF asked if the authors could enlarge on the design pressure rating of equipment designed to contain the explosive decomposition of propylene oxide.

Mr. FORSTER said that Dr. Burgoyne had done research work on this which indicated that pure propylene oxide gas phases were not explosive.

Mr. KNEALE said that block polymers were made involving the use of ethylene oxide, which certainly gave rise to explosive atmospheres. Those reactions were carried out at pressures such that in the event of an explosion the reactor would not rupture. The maximum pressure rise was about ten times.