ORIGINAL

Chemical Stopper for Runaway Propoxylation

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Propoxylation becomes important more and more for making materials of urethane foam and surfactants in industry.

The actual production of polyether polyols for urethane foam amounted to 297,750 t in 1990, and was estimated at 300,000 t in 1991.

However, propylene oxide (PO) is one of a low-boiling-point monomer which reacts so fast at high temperature, that it is very important to know how to stop propoxylation when it becomes uncontrollable. In this paper, it was proved that runaway propoxylation could be stopped with dosing phosphoric acid in reaction mass.

1 Introduction

In the previous report, an equation for maximum pressure and temperature in the runaway propoxylation was proposed¹⁾.

The pressure of runaway propoxylation could be calculated by the following numerical expression.

$$\text{Log } P = (\text{Log } C / 1.3238) - (1,066.4 / T) + 2.5040 \quad (1)$$

C : PO concentration in reaction mass (wt %)

P : abs. pressure (kgf/cm²)

T : abs. temperature (K)

And its validity demonstrated by adiabatic experiments using "Reaction Calorimeter RC-1".

It is proved distinctly that maximum pressure is not so high as believed before, but rise of temperature is in dangerous range.

If reaction temperature rises over 200°C, the TU value (terminal unsaturation, allyl and propenyl ether compounds) increases in number and the value of products decreases. And if it rises over 300°C, reaction apparatus becomes in danger. If it is possible to stop runaway propoxylation, temperature

rises not so high, and products is re-useful with low TU value. In the past, it was popular that cooling of out walls of reaction apparatus with a large quantity of falling water when it ran away. It was known well that propoxylation could not occur with neutralization of catalizer, but was not confirmed the effect of neutralization after it ran away. And scarcely any preventive

The explanation of them are as follows.

① Reactor (Autoclave) ② Jacket ③ Silicone oil tank ④ Calibration heater ⑤ Thermometer in reaction mass ⑥ Thermometer in jacket ⑦ Agitator ⑧ Platform scale for dosing ⑨ Control valve for dosing ⑩ Pressure sensor ⑪ Cooling water

Fig.-1 Apparatus of reaction calorimeter RC-1.

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Table-1 Calculated maximum pressure and temperature in runaway propoxylation.

Condition	105°C × 22 wt %	105°C × 33 wt %	120°C × 33 wt %
Abs. press. (kgf/cm ²)	7.4	14.0	16.4
Temperature (°C)	234	298	312

(Condition : 105°C × 22 wt % → reaction temperature is 105°C, and PO concentration in reaction mass is 22 wt % when Ad mode starts)

measures had been taken against runaway propoxylation. In this paper, it was proved that neutralization of catalizer, even if propoxylation already ran away, was effective to stop it by adiabatic experiments using "Reaction Calorimeter RC-1".

Catalizers well known in propoxylation are, inorganic bases^{2)~4)}, alcoholate^{5), 6)}, alumina⁷⁾, organic metal⁸⁾ and iron(III) chloride^{9), 10)}. And inorganic bases are popular most for propoxylation, we selected anhydrous potassium hydroxide as catalizer, and phosphoric acid, being less corrosive to reactor, as chemical stopper for runaway propoxylation.

2 Experimental

We used Reaction Calorimeter RC-1¹⁾. Device for propoxylation and dosing phosphoric acid for the following experiments is shown in Fig.-2.

The operation of it is as follows.

Preparation : Open valve-1 (valves-2, 3 and 4 are closed) and dose proper quantity of phosphoric acid into hopper, and close valve-1.

Operation : When propoxylation runs away, stop PO dosing first, (continue stirring) and open valves-2 and 3 with remote control, next open valve-4 in the same way.

PO concentration in reaction mass is calculated by following equation¹⁾.

$$\text{Log } C = 1.3238 \text{ Log } P + (1,411.7/T) - 3.3148 \quad (2)$$

Experimented 7 terms are as follows.

Exp. 1

Polyether polyol A (Glycerol/PO adduct, M.W. 2,000 ; 500 g), and 2.5 g (purity-accounted) of anhydrous potassium hydroxide

The explanation of them are as follows.

- 1) Valve-1 2) Valve-2 3) Valve-3 4) Valve-4
5) Hopper 6) Stock tank 7) Connected pipe
8) Reactor 9) Agitator 10) Phosphoric acid

Fig.-2 Device for dosing phosphoric acid.

(KOH) are charged in RC-1, and controlled at 105°C under stirring. After this treatment, dosing of PO is started under 0 kgf/cm², then pressure and temperature are controlled at 6.0 kgf/cm² and 105°C, and now PO concentration of reaction mass is found to be about 28 wt %. Then, PO dosing is stopped and reaction is changed to Ad mode (adiabatic mode, controlled without heat of reaction loss automatically by RC-1).

Exp. 2

Polyether polyol A (500 g), and 2.5 g of KOH are charged in RC-1, and controlled at 105°C under stirring. After this treatment, dosing of PO is started under 0 kgf/cm², then pressure and temperature are controlled at 6.0 kgf/cm² and 105°C. Then, PO dosing is stopped and reaction is changed to Ad mode. After 5 min, 2.4 g (0.5 mol equivalent) of 90 % aqueous phosphoric acid is dosed in reaction mass.

Exp. 3

Polyether polyol A (500 g), and 2.5 g of KOH are charged in RC-1, and controlled at 120°C under stirring. After this treatment, dosing of PO is started under 0 kgf/cm², then pressure and temperature are controlled at 7.0 kgf/cm² and 120°C, and now PO concentration of reaction mass is found to be about 28 wt %. Then, PO dosing

is stopped and reaction is changed to Ad mode.

Exp. 4

Polyether polyol A (500 g), and 2.5 g of KOH are charged in RC-1, and controlled at 120°C under stirring. After this treatment, dosing of PO is started under 0 kgf/cm², then pressure and temperature are controlled at 7.0 kgf/cm² and 120°C. Then, PO dosing is stopped and reaction is changed to Ad mode. After, 5 min 3.4 g (0.7 mol equivalent) of 90 % aqueous phosphoric acid is dosed in reaction mass.

Exp. 5

Polyether polyol A (500 g), and 2.5 g of KOH are charged in RC-1, and controlled at 105°C under stirring. After this treatment, dosing of PO is started under 0 kgf/cm², then pressure and temperature are controlled at 6.0 kgf/cm² and 105°C. Then, PO dosing is stopped and reaction is changed to Ad mode. After 5 min, 1.6 g (0.33 mol equivalent) of 90 % aqueous phosphoric acid is dosed in reaction mass.

Exp. 6

Polyether polyol A (500 g), 2.5 g of KOH and 2.4 g of 90 % aqueous phosphoric acid are charged in RC-1. After 2 h stirring under reduced pressure at 105°C, reaction is started under Tr mode (reaction temperature mode, controlled at fixed temperature automatically by RC-1) with dosing PO under 0 kgf/cm², then pressure and temperature are controlled at 6.0 kgf/cm² and 105°C.

Exp. 7

Polyether polyol B (produced by Exp. 2) (500 g), 3.5 g of KOH are charged in RC-1. After 2 h stirring under reduced pressure at 105°C, reaction is started under Tr mode with dosing PO under 0 kgf/cm², then pressure and temperature are controlled at 6.0 kgf/cm² and 105°C.

3 Results and Discussion

The results of Exp. 1~7 are shown in Figs.-3, 4 and -5.

Fig.-3 and -5 (Exp. 2,4) show that reaction is nearly stopped by dosing of phosphoric acid in reaction mass. And no heat of re-

action is observed in Exp. 6, neutralization of potassium hydroxide catalizer by phosphoric acid is effective for stopping of runaway propoxylation.

Proper quantity of phosphoric acid is over 0.5 mol equivalent to added potassium hydroxide. Exp. 5 shows that 0.33 mol equivalent is not enough to stop runaway propoxylation. In this case, phosphoric acid could be regarded as dibased acid.

Fig.-3 Temperature of adiabatic propoxylation.

Fig.-4 Pressure of adiabatic propoxylation.

Fig.-5 Heat of reaction (Evaluated by RC-1)

(Received June 25, 1992)

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Key Words

chemical stopper, runaway propoxylation, potassium hydroxide, phosphoric acid, Reaction Calorimeter RC-1, propoxylation, neutralization of catalizer.

暴走プロポキシレーションにおけるケミカルストッパー

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プロポキシレーションにおける暴走反応は『PO濃度式』等を活用することによってシミュレーションの可能なことは既に述べた。

それによると、最高到達圧力は従来知られていた予測法による値に比べてかなり低いことが予想され、かつ実証されたが、温度は従来法とほぼ同じレベルであり、反応条件によると 300℃ を越えることが判明した。

温度上昇による災害を防止する方法を開発することは、30 万 t を越える生産量を持つプロポキシレーションにとって重要な課題である。

従来は反応缶の外壁を大量の水で冷却することなどが提案されていたが、適当な測定装置がなかったためその効果の検証はされていなかった。

我々はカセリアルカリを触媒とするプロポキシレーションにおいてリン酸を添加する事で反応の暴走を停止できることを、『リアクションカロリメータ RC-1』を用いての断熱反応で実証した。

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