DATE: January 8, 2016

TO: DIERS Membership

FROM: Joseph C. Leung, Design/Testing Committee Chair

CC: Harold G. Fisher, DIERS Chairman

SUBJECT: DIERS Round-Robin (RR) Testing of a Phenol-Formaldehyde Reaction

The proposed RR system is a phenol-formaldehyde reaction using an alkali as catalyst. Commercial phenol-formaldehyde products catalyzed by a base are called *resoles*. We conducted an initial test with the proposed composition and procedure that gave us information regarding the severity of this runaway reaction and its peak pressure and temperature. We extend an invitation to all who would like to participate in conducting runaway reaction experiments.

SCENARIO: Adiabatic runaway resole reaction in a sealed test cell

COMPOSITION:

|  |  |  |  |
| --- | --- | --- | --- |
| Formulation | % | CAS No. | Sigma Aldrich |
| Phenol | 43.59 | 108-95-2 | 328111 |
| Deionized Water | 25.86 | 7732-18-5 |  |
| Paraformaldehyde 95%, Powder | 26.35 | 30525-89-4 | 158127 |
| 50% Aqueous Sodium Hydroxide Solution | 4.20 | 1310-73-2 | 415413 |
| Total |  |  |  |

NOTES:

1. The materials do not have to be purchased from Sigma Aldrich, but they should have the same specifications.
2. Do not premix the reactants outside the test cell because it will be difficult to handle the slurry of paraformaldehyde solids in phenol and water. Paraformaldehyde goes completely into solution only above 60°C and well after an exotherm has been detected.
3. The specific gravity of the initial mixture is about 1.25.
4. For a 111-ml test cell like a typical VSP2, the suggested sample size is 75ml, which corresponds to about 94 g of sample. For other instruments, please use the same loading, i.e., about 85 grams (68 ml) per 100 ml test cell volume.
5. The melting point of phenol is 40.5°C. Heat phenol to at least 50°C for the charge. If the source of phenol is a large bottle, the contents do not have to be completely molten. It suffices to have enough material for the test.
6. In the preliminary VSP2 experiment the peak temperature and pressure were 257°C and 645 psia (44.5 bara). Under these conditions there is no hazard of decomposition of the runaway mass. Other than inert gas present, the pressure rise is entirely due to vapors.
7. Even though the system is tempered, the cooldown pressure may be slightly higher than the initial pressure. This might be the result of unreacted formaldehyde left in the test cell. In the preliminary test the initial pressure was 2.5 psia (0.17 bara) and the final pressure was 5.9 psia (0.41 bara).
8. The self-heating and self-polymerization rates may be slightly erratic in the vicinity of the peak exotherm. This is normal because the mass will be completely gelled at that stage of the reaction.
9. **VERY IMPORTANT:** Make sure to cool the phenol-deionized water-paraformaldehyde mixture in the calorimeter below 20°C before charging aqueous 50% sodium hydroxide solution. An exotherm may be detected at 30°C, so it is important to keep the test cell below this temperature before the test begins.

PROCEDURE

1. Program a Heat-Wait-Search sequence as follows: Start with a search temperature of 30°C, 5°C increments, 20-minute hold period per search and final search temperature of 60°C. If the exotherm does not initiate by 60°C, something is wrong with the materials or with the setup or the instrument. Use a self-heating rate ≥0.1°C/min as the criterion for exotherm detection. Set the exotherm limit at 400°C, but the experiment should end at a much lower temperature. Program the experiment to keep the test cell closed throughout the run including the cooldown.
2. Charge phenol to the test cell.
3. Charge deionized water to the test cell. About 10% of the water amount may be held back if the charge line has to be rinsed.
4. Charge 95% paraformaldehyde powder to the test cell.
5. Charge 50% aqueous sodium hydroxide solution to the test cell. Rinse the line with the remainder 10% of deionized water, if applicable.
6. Assemble the test cell in the calorimeter and follow the steps below without delay.
7. Perform twice the following procedure: Inert the test cell by pressurizing to 30 psia (2.1 bara) with nitrogen and then venting to 16 psia (1.1 bara).
8. Evacuate the test cell to 2 to 3 psia (0.14 to 0.21 bara).
9. Initiate the experiment.
10. Make sure the instrument switches to adiabatic mode once an exotherm has been detected.
11. Allow the exotherm to proceed until it ends as determined by a sudden drop in self-heating rate and self-pressurization rate.
12. Allow the contents to cool down to room temperature before discharging.

ITEMS TO SUBMIT:

1. Information about sample size, instrument used and any unexpected findings.
2. Submit data in Excel format, showing time t (min), temperature T (°C), pressure P (psia or bara), self-heating rate dT/dt (°C/min) and self-pressurization rate dP/dt (psi/min, or bar/min) with clear header identifying each column.
3. Submit data plots showing T (°C) and P (psia or bara) vs time (min), dT/dt (°C/min) and dP/dt (psi/min, or bar/min) vs -1000/TK Arrhenius-type plots, and log10 P vs -1000/TK chart display.

QUESTIONS – please direct your inquiry to:

1. VSP2 users – Tom Olechnowicz (TOlechnowicz@ashland.com)
2. APTAC users – Enio Kumpinsky (ekumpinsky@ashland.com)
3. ARSST users – Gabe Wood (Wood@fauske.com)

THANK YOU ALL.

Deadline for Submission: March 11, 2016

Send data or inquiry to: Joseph Leung at the following e-mail: leunginc@cox.net

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