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Interoffice Communication

To V. E. Messick, Aberdeen, Mississippi

From J. E. Nickerson and R. D. Melling, Ponca City, Oklahoma

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Subject AMS Emergency Kill System

Recently an Aberdeen reactor was killed using the AMS Emergency Kill System. Recovered VCM from that batch was collected in an empty recovered monomer receiver to segregate it from normal recovered monomer. The recovery system was then switched back to collecting monomer in the normal receiver and another reactor was steam stripped. Several of the next batches charged showed signs of AMS contamination. Apparently, the normal recovered monomer had become contaminated indicating all the Emergency Kill AMS had not been collected in the contaminated monomer receiver.

We think that the AMS is stripped fairly completely from the reactor during steam stripping but then is condensed in the recovery knockout pots and compressor seal water systems forming a separate liquid layer. This separate layer is then slowly flashed into the monomer vapor during subsequent recoveries. Equilibrium flash calculations at normal recovery system operating conditions indicate the AMS will be stripped from the recovery system at the rate of about two pounds AMS per 1,000 pounds recovered VCM. This would indicate several recoveries would be required to purge the recovery system of the 200 to 300 pounds AMS injected into a reactor during emergency kill.

Normal practice for handling contaminated monomer has been to segregate contaminated monomer and slowly blend it back into the system at rates known to have minimal effects. This segregation is difficult at best because of condensation in the knockout pots and would be almost impossible if several reactors would have to be killed at the same time. There would be no place to put all the contaminated monomer. Aberdeen has requested that a procedure for handling large quantities of AMS contaminated material be developed to minimize the impact of this important safety system on subsequent plant operations. Several ideas based on neutralizing or removing AMS from the system are discussed below.

1. Possibly the best way of handling AMS is to deal with it before it can contaminate the recovery system.

    a. Many process monitoring devices, automatic controls, and operating procedures are employed to safely control the polymerization reaction. If all causes of over pressure were known and could be prevented, then the Emergency Kill system would not be needed and contamination could be avoided by not adding AMS to the reactor. However, there is always the possibility that an unanticipated problem can occur. The Emergency Kill system is

an extremely important safety system and cannot be safely deleted. It must be available for use in an emergency and a procedure must be developed to adequately handle the quantities of AMS involved.

b. Another way of avoiding AMS contamination would be to use some other killing agent, one that did not cause contamination problems. Several killing agents were evaluated before setting the basis for the Emergency Kill system designs; none were found to be more effective than AMS in situations where both cooling and agitation were lost. Some had other problems such as being in solid form which required slurries. The search for newer and better killing agents should continue but for now we need to learn to deal with AMS.

c. Large quantities of AMS were used in LRPP tests to develop the design basis for the plant AMS Emergency Kill systems. The excess AMS was handled by reinitiating the batch with one to two pounds of initiator per pound of AMS. The resulting resin was not Type I quality but could probably have been easily blended. Reinitiating a batch after emergency kill would probably be the easiest way of handling excess AMS. Initiator could be added in several small steps until the reaction restarted. However, there would always be concern about the amount of initiator required.

d. Another idea would be to first recover vinyl without steam stripping, then reinitiate to deactivate the AMS, then complete steam stripping. Some AMS would be carried over with the recovered VCM but the quantity would be tremendously reduced and could be easily handled in the normal manner. This procedure would minimize the quantity of off-spec resin because of the limited amount of vinyl in the reactor. However, there are still questions about how to determine how much initiator to use, and what happens if too much or too little initiator is used. Dean Wiemer has indicated that it might be possible to use a cheap water soluble solid inorganic initiator such as potassium persulfate which would reduce the possibility of initiator carryover into the recovery system.

2. A second way of reducing contaminated monomer problems is to recover the emergency killed batch as normal but deal with the condensed AMS in the recovery system.

a. The possibility of reacting or neutralizing the AMS in the recovery system was discussed with R&D. Several reactions were discussed but none could be identified that could be safely handled in a system not designed to control the reaction.

b. All liquid in the recovery system could be drained to a separation vessel where the water phase could be decanted to the water stripper and the AMS phase sent to the incinerator.

c. All liquid in the recovery system could be drained through a carbon bed or molecular sieve to absorb the AMS. Water would be returned to the water stripper. The carbon bed or molecular sieve could then be disposed of in a landfill or regenerated for reuse. Regeneration could be handled by steam stripping to the incinerator or by reacting the AMS.

d. The recovery system liquid could be drained to a segregated VCM receiver to allow the AMS layer to dissolve in the vinyl. The water layer would be drained to the water stripper. The contaminated vinyl would then be very slowly blended back into the system.

3. A third way of dealing with contaminated monomer would be to purify the recovered monomer before charging it to a reactor.

a. Contaminated recovered monomer could be incinerated to avoid contaminating the whole reactor area. This would obviously not be economical and there is not enough incinerator capacity for this anyway.

b. The possibility of reacting AMS in vinyl was discussed with R&D. Again, no reaction was identified that could be safely controlled in the available process equipment.

c. Fractionation equipment could very easily separate AMS from vinyl. Fractionation could also remove light ends and reduce reactor venting requirements. However, capital and operating costs would be high.

d. It might also be possible to selectively absorb AMS from vinyl with a carbon bed or molecular sieves. Again, capital dollars would have to be spent.

Of all the ideas presented, item 1.d. probably has the most potential. This idea was to partially recover the unreacted monomer, reinitiate to deactivate the excess AMS, then complete the recovery with steam stripping. This procedure would require no capital money and could be implemented immediately if needed. Affects on resin physical properties should be minimal due to the small amount of vinyl left in the reactor.

Using too little initiator would result in not all of the AMS being deactivated, but AMS carryover would be significantly reduced and should be much easier to deal with. Using too much initiator could allow initiator carryover into the recovery system and would reduce resin quality. In this case the hydroquinone injection should prevent vinyl polymerization but this is dependent on the hydroquinone system working correctly. Use of potassium persulfate or other water soluble initiator for reinitiating the reactor batch would greatly reduce the initiator carryover problem.

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