Air Products

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14 December 1978

Mr. G. Baise
Beveridge, Fairbanks & Diamond
One Farragut Square South
Washington, D.C. 20006

Dear Gary:

Enclosed is a statement prepared by Nick Wheeler as a response to the request by Goodwin, et. al, for a list of things that cause relief valve discharges.

I also enclose a slightly edited version, where I suggest omitting a list of operator errors. This is my version. I could not get a hold of Bob Laundrie to get his comments.

As we discussed on the phone, you could dress this up, add some more arguments, and include the paragraph from Dow as a useful part of any revised enforcement letter. We gave that paragraph to Susan, and as Scott will remember, agreed to a qualification that the operator should be in compliance with the model plant or its equivalent.

Please use these as you see fit.

Very truly yours,

John T. Barr

JTB/sjw
Enc.

cc: R. Laundrie - General Tire
R. N. Wheeler - Union Carbide

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R. N. WHEELER, JR.

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Emergency relief devices in the VC/PVC industry consist of the following three items permitted by the EPA Vinyl Chloride Emission Standard:

1. Rupture disks are thin metal diaphragms which are fabricated to burst at a pre-designed pressure thus releasing the vessel contents and preventing vessel over pressure. They, while simple in concept, and leak-free, are precision devices subject to premature failure for a variety of reasons. After bursting, a rupture disk must be manually valved off to conserve the vessels contents.

2. Relief valves, in their simplest form, .onsist of a nozzle covered by a metal plate held in place by a spring. When the vessel pressure in the nozzle exceeds the force of the spring holding the disk in place, the disk raises off the nozzle permitting the excess pressure to escape from the vessel. When the excess pressure has been released the spring forces the disk back on the nozzle theoretically closing in the vessel. In actual practice the re-setting or closing is very seldom leak-free thus the valve must be serviced, i.e. the nozzle and disk cleaned and reseated manually.

3. Manual relief valves are simply hand or remotely operated shut off valves which are manually activated to relieve excess vessel pressure and manually closed.

Combinations of these devices are often used to improve vessel tightness and to attempt to offset the faults of one type with the advantages of the other.

The function of an emergency relief device is to prevent vessel over pressure which may lead to structural damage of the vessel or in the worst case an explosive rupture of the vessel which could cause loss of life, fire, major property damage and major releases of vinyl chloride monomer.

The section of a relief device and its size is based on engineering judgment following an evaluation of the following reactors:

1. The magnitude of an uncontrollable chemical reaction, or in the case of PVC manufacture, an uncontrollable polymerization.

2. Heat uptake resulting from exposure of the vessel to an external fire.

3. Loss of services, i.e. cooling water, electricity, control power, steam, etc.

4. Mechanical failure of the vessel's operating equipment.

5. Malfunction of the vessel's operating equipment.

6. Operating personnel errors.

7. Emission control regulations.

In the case of a PVC reactor the uncontrollable reaction factor is so large compared to other items, it is the primary basis for relief device selection. In the strictest sense anyone of the remaining six items can lead to an uncontrollable polymerization as well as cause an emergency relief device activation on its own.

Much effort has been put into the design of plants with auxiliary power and cooling water supplies, alarms, control system interlocks, reactor short stop systems, computer control, gas holders and so forth. Operators for this process are highly trained. Detailed operating and emergency procedures are written and made available to them. All these contribute to improved control and elimination of emergency releases; however, there are areas where redundancy is not possible and the possible improvement costs far more than its potential or probable benefit.

Some items which singly or in combination with other items can cause emergency releases are:

1. Uncontrollable Reactions

   A. Variations in raw material quality. A reactor's contents may simply coagulate or the polymerization rate increase to much greater than normal.

   B. Variations in the oxygen content of the reactor or its charge.

   C. Emission control regulations, e.g. the operator may try to run one more batch in a fouled reactor in order to meet the reactor opening emission limits. Also, when relief valve discharges are manifolded into a vent to a control device, emergency relief from one reactor can destroy or render relief valves on other reactors inoperative through excessive fouling and/or back pressure. Excessive back pressure on a relief valve can blow the bonnet off carrying with it the spring and disk.

2. Exposure of the Vessel to an External Fire

   A jacketed reactor with full cooling water on and agitator running seems at first glance protected against external fires and it is until the fire melts control leads and power wire insulation. A small fire of surprisingly short duration can effectively destroy all or most of a reactor control system.

3. Loss of services, i.e. Power, Cooling Water, etc.

   A. Redundant power systems usually mean two separate sources of power but no plant has duplicate motor control centers, duplicate motor wiring or duplicate motors.

   B. Sub-freezing weather is the bane of the plant operators existence. Control leads, air lines, water lines and inert gas lines freeze or plug with ice. Floating ice in the river plugs cooling water intakes. Water cooled mechanical seals split open. Electric motors won't start or stop due to ice in the starters. Valve operators can become frozen in place.

   C. Excessively hot weather can cut operating safety margins to nil due to high cooling water temperatures.

D. Mechanical failures of service facilities equipment. The effect is similar to that from operating equipment failure in terms of frequency and variety. This will be discussed in detail later.

4. Mechanical Failure of Operating Equipment

Metal fatigue, corrosion (internal and external), stress corrosion cracking, gasket failure, mechanical damage, power insulation failure, and wear are the primary causes of equipment, vessel and piping failures. A good preventive maintenance program can prevent most of the wear failures and to a limited extent, the internal and external corrosion failures. Critical pumps and compressors can be dualized or spares installed. Mechanical failures not covered by such a program are simply undetectable and therefore unpreventable by ordinary methods.

For example, a reactor agitator system is made up of many parts and assemblies subject to failure. The motor has a starter replete with fuses and relay switches, power wiring from the feeder to the starter, power wiring from the starter to the motor, and control wiring from the starter to the switch on the operating floor. The motor has two antifriction bearings, a cooling fan, stator coils and a rotor mounted on a shaft. The motor shaft is keyed to a mechanical coupling which is also keyed to the speed reducer input shaft. The speed reducer has a half dozen antifriction bearings, three or four precision cut gears each keyed to a shaft, a lubrication system and an output shaft which is attached to another mechanical coupling. This mechanical coupling is keyed to the agitator shaft. The agitator shaft supported by at least two antifriction bearings passes through the reactor wall via a dual mechanical seal. This mechanical seal is serviced by a cooling system and a sealing lubrication fluid system. If the agitator shaft is very long an internal bearing is mounted in the bottom of the reactor. This internal bearing has another flush and lubrication system. The agitator also has one or more impellors mounted on the shaft. Additionally, there are many small system parts which are subject to failure.

Loss of agitation during a PVC polymerization immediately creates an emergency situation. Cooling rate drops precipitiously. Short stop addition is much less effective. The monomer may quickly become a five ton resin lump.

Despite all the obvious possibilities of agitator mechanical failure, such failures occur very rarely. For EPA, however, to insist that such failures and resulting emergencies are totally preventable and/or controllable is unrealistic.

Some other mechanical failures which have caused emissions:

1. Rupture disk, damaged in ordinary service or installation.
2. Rupture disk fatigue.
3. Rupture disk corrosion.
4. Rupture disk delamination.
5. Relief valve spring failure.
6. Agitator dropped off drive shaft (chloride stress corrosion of studs).
7. Coolant pump failed.
8. Motor valve froze shut.
9. Computer failure over charged reactor.
10. Temperature control lead shorted.
11. Temperature controller reset inoperative.

12. Alarm system failed.
13. Stainless steel charge line cracked.
14. O-ring in mechanical seal failed.
15. Mechanical seal carbon cracked.
16. Painter broke temperature transmitter.
17. Water in instrument purge gas.
18. Reactor stuffing box water jacket cracked.
19. Reactor top head cracked due to stress corrosion cracking.
20. Short stop line plugged.
21. Computer deprogrammed itself.

5. Equipment or Control Malfunction

The plant designer and/or operator must make an engineering judgment between the amount of automation that best fits his process and his operating procedure. The greater the complexity, and therefore possibility of failure of the instrumentation, while more manual operations can lead to more operator errors.

A completely automated plant would give the nearest approach to our operator-error-free plant, yet even these have been found to be subject to massive computer failure with immense resultant potential for emissions.

6. Operator Errors

Human beings are complex creatures. On occasion they out perform the most complex computer because they can think. On other occasions they fail to handle the simplest task correctly, possibly because of preoccupation with a personal problem.

We do not believe that it is appropriate to cite an individual operator who has made an inadvertent error after a long period of careful and conscientious service, and certainly it is less appropriate to penalize his employer, for something completely out of the control of the employer. Each emission, whatever the cause, should be evaluated individually to determine if it occurred as the result of an event not controllable by an owner or his representative who was in compliance with a model plant equivalent operation. Certainly one of the judgment criteria should be the frequency with which such events have occurred at that plant. Discussion of relief devices and causes for their activation is not intended to be complete and it can in no way be used to define permissable or non-permissable relief valve emissions. The intent is to demonstrate to EPA that the whole subject is a very complicated one and that emission regulation is not a simple black and white situation.