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A Method to Identify the Chemical Hazards of Tasks Derived from Abnormal Conditions of Processes

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Abstract

Hazards, which were resulted from operation of improper tasks derived from process abnormal conditions, cannot be identified effectively by the traditional hazard identification methods, such as HAZOP and JSA. A method based on the hazardous information of chemicals to identify the hazards of tasks derived from abnormal conditions of processes was proposed. A checklist for the intrinsic chemical hazard identification and a worksheet for the process/task hazard identification were included in the proposed method. The intrinsic hazards of chemicals can be identified based on the hazardous information of chemicals, such as those provided on SDS. Combining with the enabling condition of the chemical hazards and the possible tasks derived from process abnormal conditions, the tasks derived from process abnormal conditions, which will supply the condition of initiating the chemical hazards, were identified. Based on the identified tasks, the potential hazards of the tasks can be identified by a pre-designed worksheet, and the safeguards and the suggestions can be identified. An example of using the proposed method to identify the hazards of tasks derived from process abnormal conditions was included in this manuscript.

Introduction

An explosion accident resulted in one fatality and one injury occurred in an acrylic manufacturing process, in Miaoli, Taiwan, on December 7, 2015 [1, 2]. The incident investigation indicated that the feed pipe of benzoyl peroxide (BPO) was knocked by a mallets to let the BPO go into the reactor smoothly because the workers believed that BPO was stuck in the pipe, although the fact is that the inlet valve was not opened. It is reported in Safety data sheet (SDS) that the BPO is explosive in presence of shocks [3].

Knocking the feed pipe stuck with BPO, as mentioned above, is not a normal operation, it is a trouble shooting task derived out due to abnormal condition of BPO being unable to feed into the reactor. Since the trouble shooting tasks, such as the case of feeding the BPO into the reactor smoothly, are seldom encountered, the safe operating procedure for such tasks are always not included in the standard operating procedure. The operating steps of trouble shooting are always focused on how to remove the troubles faced, safety review is not the priority and is always ignored. If the hazards of the tasks derived from abnormal conditions of processes could be identified beforehand, the safe precautions would be developed and the operators be trained in such safe precautions, then the accidents derived from such tasks could be prevented.

Hazard and operability study (HAZOP), failure mode and effects analysis (FMEA) and What-If analysis are three recommended methods in process hazard analysis by Occupational Safety and Health Administration (OSHA) [4] of USA and Hazardous Workplace Review and Inspection Rules [5] of Taiwan, and HAZOP is the most frequently used method in hazard identification in Taiwan. However, the explosion hazard of BPO as mentioned above cannot be identified by the three methods. The shock is not adopted in the process deviation of pipe in HAZOP analysis, traditionally, and this deviation will not be assessed in the execution of HAZOP. Similarly, the feed pipe stuck with BPO is not a failure mode of FMEA, and this scenario will not be evaluated. For the situation of BPO being unable to enter the reactor, the consequence is always focus on the impact of no flow of BPO, the reaction cannot be proceeded, and is not take into account the impact of tasks derived from removing the trouble of no flow of BPO, either for the process deviation of no flow in HAZOP analysis or in What-If analysis. Knocking the feed pipe of BPO is not a regular process, it is just a task of trouble shooting derived from an abnormal condition of processes, and it is not taken into account in the HAZOP, FMEA and What-If analysis. Job safety analysis (JSA) is usually used in the hazard identification of operating procedures. However, the accident mentioned above cannot be identified by the JSA, because the task of knocking the feed pipe of BPO is derived from abnormal condition and is always not included in the standard operating procedures and thus is not analyzed by the JSA. The fact we have to recognize that the potential hazards of tasks derived from abnormal conditions cannot be identified by the tools of traditional hazard identification. Unfortunately, many accidents were resulted from these tasks because the operating steps are always determined without safety review in the situation of emergency. A method to identify the hazards of tasks derived from abnormal conditions of processes is necessary in practical, and is proposed in this study.

The method

The chemical hazards will be initiated and result in an incident only if under certain specific conditions, such as decomposition of hydrogen peroxide only occurred at temperatures being high enough. That means the occurrence of chemical incidents need an enabling condition to initiate the chemical hazards. To identify the occurrences of chemical hazards of processes or tasks, the importance of identification of the enabling condition is as well as that of identification of the intrinsic hazards of chemicals. A checklist, as shown in Table 1, was designed to identify the intrinsic hazards of highly hazardous chemicals used in processes and tasks which will supply the conditions to initiate such chemical hazards while derived from abnormal conditions of processes. The final purpose of this method is loss control of the chemical hazards, thus, a worksheet, displayed in Table 2, was designed to identify the hazards of the derived tasks and to prevent and/or minimize the consequences of the hazards. After completing Table 1, the intrinsic hazards of chemicals and which tasks or processes are possible to supply the enabling condition were identified, the next step is to identify the hazards of the derived tasks or processes and the necessary safeguards by Table 2.

The intrinsic hazards of chemicals

The purpose of the checklist of the intrinsic hazards of chemicals (Table 1) is to identify which tasks or processes may supply the enabling conditions to initiate the intrinsic hazards of chemicals. Before identifying these tasks or processes, the intrinsic hazards of chemicals need to be identified. The intrinsic hazards of chemicals considered in this method include toxicity, flammability, and reactivity. In this method, poison and corrosion are regarded as the consequences of the toxic hazard, i.e., corrosion is included in the toxic hazard. Fire and explosion are the consequences of the flammable and reactive hazards.

SDS and other information associated with the chemical hazards are necessary in the identification of the intrinsic hazards of chemicals. SDS is the minimum required information. It should be very careful that the hazards provided by the SDS always based on the condition of normal temperatures and normal pressure [6]. However, the operational conditions are always different from normal condition. Since the hazards of chemicals may be different for different condition, such hazards in the possible operational conditions should be identified. One example is that o,o-dimethyl phosphoramidothioate (DMPAT) is stable at normal temperatures and normal pressure but decomposes at temperature greater than 93.5°C [6].

Table 1 Checklist for the intrinsic hazards of chemicals

Chemical: Process:				
Intrinsic Hazards of Chemicals	Yes	No	Description	Tasks/Processes Supplying the Enabling Conditions
Toxicity	☐	☐	1. ☐ Fatality 2. ☐ Acute toxicity Explanation: 3. TLV-TWA: 4. ☐ Corrosion Explanation: 5. ☐ Others: 6. Routes entry: ☐ Skin; ☐ Eye; ☐ Inhalation; ☐ Ingestion	
Flammability	☐	☐	1. ☐ Flammability limits (vol.%): 2. ☐ Flash point (°C): 3. ☐ Auto-ignition temperature (AIT) (°C): ☐ AIT < room temperature ☐ AIT < process temperature 4. ☐ Dust explosion Flammability limits (kg/m^3): 5. ☐ Others:	
Reactivity	☐	☐	1. ☐ Decomposition Onset temperature (°C): Decomposition products/hazards: 2. ☐ Polymerization	

			Onset temperature (°C): 3. ☐ Incompatibility Incompatibility with various substances: Incompatibility with various substances in plant: 4. ☐ Sensitive to shocks 5. ☐ Others:	

Table 2 Worksheet for the process (task) hazards

Chemical:

Process:

Item	Hazard Classification	Hazard Description	Tasks/ Processes Derived from Abnormal Conditions	Cause Deriving out the Tasks/ Processes	Consequence	Cause of Deviation	Safeguards	Is the protection sufficient?		Comments and Suggestions
								Yes	No	
								☐	☐	
								☐	☐	
								☐	☐	
								☐	☐	
								☐	☐	
								☐	☐	

Any intrinsic hazard of concerned chemical should be marked and be described in the field of Description. The properties characterize the intrinsic hazards of chemicals are displayed and prompted in the field of Description. For the case of toxic hazard, fatality, acute toxicity, and corrosion are highlighted, in addition to the threshold limit value – time weighted average (TLV-TWA) value is required. If the acute toxicity or corrosion exists, the details may be described, if necessary. Other toxic hazards or any information useful to assist in understanding of the toxic hazards can also be described. As mentioned above, one of the purposes of the checklist is to assist in identification of the tasks or processes may supply the enabling conditions, the routes entry for the concerned chemical was required.

For liquids and gases, the values of flammability limits, flash point and auto-ignition temperature (AIT) are required to be filled in, if the flammability hazard existed and these values are available. It is also encourage to fill in the values for solid chemicals, if any of these values are available. The checklist also prompted that whether the AIT is less than room temperature or process temperature in order to identify the fire and explosion hazards for the leakage. For solid particles, the dust explosion is taken into account. If the dust explosion hazard exists, the flammability limits are required. Other flammable hazards can also be described.

The reactivity hazards considered the reactivity of the pure substances and the incompatibility of the concerned chemical with the possible chemicals. Decomposition and polymerization reactions are taken into account for the reactivity of the pure substances. The onset temperatures of the decomposition and polymerization are required in order to identify possible tasks or processes, which will supply temperatures being greater than the onset temperature, if possible. If decomposition reactions produce toxic or flammable materials, it is suggested to write down the decomposition products in order to consider the secondary disaster. The incompatible materials existed in the plant with the concerned chemical were required to be identified. In addition, whether the concerned chemical is sensitive to shocks was required to be identified. As the cases of toxic and flammable hazards, other reactive hazards can also be described.

The detailed cause of the hazards is not the focus of the analysis of the intrinsic hazards of chemicals; which condition will initiate the hazards is just the focus. Take example of high temperature resulting in thermal explosion for the reactive materials, which cause, decomposition, polymerization, or oxidation, resulted in explosion is not the key-point, which tasks or processes may supply a high temperature condition to initiate the thermal explosion is just the key-point.

In addition to identify the intrinsic hazards of chemicals, the other and more important purpose of the checklist is to identify which tasks or processes may supply the enabling condition. Based on the enabling condition of initiating the intrinsic hazards of chemicals, the analyzers should think which tasks or processes may supply such an enabling condition, and write down the identified tasks or processes in the column of Tasks/Processes Supplying the Enabling Conditions. The enabling conditions are always different for different intrinsic hazards of chemicals, thus, the identified tasks or processes are always different for different intrinsic hazards of chemicals. Write down the identified tasks or processes in the field of corresponding intrinsic hazards of chemicals.

Two examples are given below for thinking which tasks or processes may supply the enabling condition. Take the first example of a raw material, which will decompose violently at high temperatures, it should be thought which tasks or processes, including be derived out from abnormal condition, may supply the condition of high temperatures. One situation is that crystallization of the raw material at low temperature derives out the heating process for such a material. The failure of heating system, irrespective of operational error or failure of the temperature control loop, will resulted in high temperatures. Since the accidents always occurred in the conditions of safeguard unavailable, the worst condition should be taken into account. The other example is for a solid particle material with sensitive to shocks, such as BPO, the analyzers should think which abnormal conditions may derive out the shocking of such a material. One situation is that such a solid material sticking in the feed pipe may make the operators to knock the feed pipe, intuitively, in order to operate smoothly.

Since the hazards attributed to the process deviation from the standard condition and the hazards in the tasks with standard operating procedure can be identified by the HAZOP and JSA analysis, respectively, this proposed method is suggested to focus on the tasks or processes, that is unable or not easy to be analyzed by HAZOP or JSA, such as those derived from abnormal conditions of processes, although this method can identify the hazards of normal operations. Therefore, it is suggested only to write down the tasks or processes in absence of analysis by HAZOP and JSA.

The process (task) hazards

After completing the checklist of the intrinsic hazards of chemicals, the tasks or processes, which may supply the enabling condition to initiate the hazards of concerned chemicals, will be identified. However, whether the protection is enough was not identified. The worksheet of process (task) hazards of this method is used to assist in analyzing how to prevent or minimize such chemical hazards.

As mentioned above, the conditions to initiate the chemical hazards are always different for different types of chemical hazards. The hazards of tasks or processes supplying such conditions are analyzed, respectively, for different types of chemical hazards; and the hazard classification, toxicity, flammability, and reactivity, should be marked in the column of the worksheet. The hazardous information identified in the column of Description of checklist of intrinsic hazards of chemicals can be copied or described more detailed to the column of Hazard Description of the worksheet of the process (task) hazards to prompt the intrinsic hazard of the concerned chemical. Copy the identified tasks or processes in field of Tasks/Processes Supplying the Enabling Conditions of the checklist to the field of Tasks/Processes Derived from Abnormal Conditions. The column of Cause Deriving out the Tasks/Processes is filled in with abnormal condition deriving out the task, such as crystallization of raw material deriving out the heating process.

Write down the developing sequence of the impact of the intrinsic hazards of the concerned chemical from the initial event for the identified task in the column of Consequence. All the possible consequences, including the worst consequence and the other ones, are suggested to be described. Since the disasters always happened in the situations of safeguards unavailable, the safeguards should be assumed to be unavailable in the identification of the consequence. In addition, the consequences, occurred everywhere, should be taken into account. The impact, such as fatalities and injuries of people, rather than consequence, such as fire and explosion, should be described. Consequence is just an intermedium sequence, and impact is actually the final results. It is suggested to describe the detailed sequence of the events from the initial event for the identified task or process to the final impact, since it can assist in identifying the safeguards and suggestions from the initial event through the intermedium sequence to the final impact.

Some derived tasks/processes initiate the chemical hazards without requiring any deviation. However, others initiate such hazards only in the situation of process deviation. In the case of knocking the feed pipe of BPO to let the stuck BPO enter the reactor, the explosion will occur while knocking the pipe, no deviation is necessary. For the case of heating a reactive material to remove the crystallization of such a material, only the failure of heating system may result in thermal explosion; the deviation of high temperature is necessary. If the deviation is necessary, fill in the column of Cause of Deviation with the deviation and the cause of such a deviation. Otherwise, fill in with “none”.

The column of Safeguards need to be filled in existing safeguards, including engineering and management controls. The function of safeguards includes prevention of the hazards occurrence and mitigation of the hazards consequences. Based on the existing safeguards, it is required to judge whether the protection is sufficient. Some tips, asking the following questions, are useful in the judgement:

(1). Are there corresponding measures for all the consequences and causes of deviations?

(2). If alarm is a safeguard, do the corresponding measures include action plans?
(3). Is the risk acceptable?
(4). Are the reliabilities of the safeguards acceptable?
(5). Can the derived task prevent the occurrence of the hazards?

If the protection is insufficient, comments and suggestions are necessary. Both the management and engineering controls are suggested. The fourteen elements of process safety management, as suggested by OSHA [4], are recommended, but not limited, for the management control, if they are applicable. The suggestions of management, such as safe precautions, safe operating procedure of trouble shooting, training of safe precautions or safe operating procedure, are useful. The information filled in the column of Consequence can be used to assist in proposing suggestions. As mentioned above, the detailed sequence of the events from the initial event through the intermedium sequence to the final impact were described in the column of Consequence, the lack of safeguards in each step can be identified and useful suggestions can be included for the steps of lacking safeguards. These suggestions include elimination of the initial events, protection measures of avoid evolution from initial event to consequence, and diminishment of the consequences.

Case study

The BPO explosion accident mentioned in section INTRODUCTION was selected as a case study, and BPO is the studied chemical. The checklist of intrinsic hazards of chemicals was completed based on the information of SDS provided by Science Lab [3], and was shown in Table 3. Table 3 indicated that there are toxicity, flammability, and reactivity hazards for the BPO. This case study was focused on the accident, thus, the characteristic of sensitive to shocks of reactivity hazard was the spotlight. The SDS indicated that BPO may self-reactive under conditions of shock [3]. In the affected plant, BPO was used as an initiator, and was feed to the reactor through a pipe by gravity. In the normal operation, the conditions of shock do not exist for BPO. In practice, the BPO in the conditions of shock is only occurred at the situation of knocking by the operators due to BPO being stuck in the pipe and unable to enter the reactor. More clearly said, the operators knock the pipe stuck with BPO to let the BPO enter the reactor smoothly. The abnormal condition of process is BPO cannot enter the reactor, the derived task is knocking the feed pipe of BPO to let the BPO enter the reactor smoothly, and the derived task supply the enabling condition, shocking condition, to initiate the reactivity hazard of BPO. The abnormal condition and the derived task were described in the field of Tasks/Processes Supplying the Enabling Conditions corresponding to reactivity hazard.

Since this case study focused on the accident, Table 4 only displayed the related part of the completed worksheets of process (task) hazards for reactivity hazards. The relative information of the accident were filled in the fields of Hazard Classification, Hazard Description. The identified derived task and the abnormal condition were filled in the fields of Tasks/Processes Derived from Abnormal Conditions and Cause Deriving out the Tasks/Processes. The consequence of knocking the BPO is that BPO will explode and resulted in casualties, properties damages and processes interruption. Since the BPO will explode in the presence of shocks without need any deviation, the field of Cause of Deviation was filled in “none”. There is not any safeguard for this hazard, thus, “none” was filled in the field of Safeguards. Since the tasks or processes derived from abnormal conditions always not identified, the safeguards for the hazards of such tasks or processes are always lacked. It is apparent that the protection of this hazard is not sufficient. There is not any prevention and protection measure for this hazard, thus, the suggestions were given in the column of Comments and Suggestions.

Conclusions

The chemical hazards of tasks/processes derived from abnormal condition of process cannot be identified by the traditional hazard identification method, such as HAZOP and JSA. A method to identify such chemical hazards was proposed. One checklist to identify the tasks or processes supplying the condition to initiate the intrinsic hazards of chemicals and one worksheet to identify the hazards of such processes (tasks) were developed to assist the hazard identification. One explosion accident attributed to the knocking of feed pipe stuck with BPO was used as a case study. This proposed method can be used in identification of the hazards of tasks/processes derived from abnormal conditions of processes and give useful suggestions. In addition, the chemical hazards during the normal operations can also be identified by this proposed method.

Table 3 Checklist of the intrinsic hazards of chemicals for BPO

<table>
<tr><td colspan="5">Chemical: BPO
Process: Acrylic Manufacturing Process</td></tr>
<tr><td>Intrinsic Hazards of Chemicals</td><td>Yes</td><td>No</td><td>Description</td><td>Tasks/Processes Supplying the Enabling Conditions</td></tr>
<tr><td>Toxicity</td><td>■</td><td>□</td><td>1. □ Fatality
2. ■ Acute toxicity
Explanation: Acute oral toxicity (LD50: 7710mg/kg)</td><td></td></tr>
</table>

			[Rat] 3. TLV-TWA: *5mg/m*^{3} 4. □ Corrosion Explanation: 5. □ Others: 6. Routes entry: ■ Skin; ■ Eye; ■ Inhalation; ■ Ingestion	
Flammability	■	□	1. □ Flammability limits (vol.%): 2. □ Flash point (°C): 3. ■ Auto-ignition temperature (AIT) (°C): *80℃* □ AIT < room temperature □ AIT < process temperature 4. □ Dust explosion Flammability limits (kg/m^{3}): 5. ■ Others: *Flammable in presence of combustible materials*	
Reactivity	■	□	1. ■ Decomposition Onset temperature (°C): *103℃* Decomposition products/hazards: 2. □ Polymerization Onset temperature (°C): 3. ■ Incompatibility Incompatibility with various substances: *acids, alkalis, combustible materials, metal* Incompatibility with various substances in plant: 4. ■ Sensitive to shocks 5. ■ Others: *Explosive in presence of heat;* *Instability temperature: > 75℃*	*1. If the BPO stuck on the feed pipe, the operators will knock the feed pipe to let the BPO enter the reactor smoothly.*

Table 4 Worksheet of the process (task) hazards for BPO

Chemical: *BPO*
Process: *Acrylic Manufacturing Process*

Item	Hazard Classification	Hazard Description	Tasks/ Processes Derived from Abnormal Conditions	Cause Deriving out the Tasks/ Processes	Consequence	Cause of Deviation	Safeguards	Is the protection sufficient?		Comments and Suggestions
								Yes	No	
1.	*Reactivity*	*Explosive in presence of shocks*	*Knocking the feed pipe of BPO to let the BPO enter the reactor smoothly*	*BPO stuck on the feed pipe*	*BPO will explode, and resulted in casualties, properties damages, and process interruption.*	*None*	*None*	☐	■	*1. Reduce the concentration of BPO from 98% to 75% to prevent the probability of explosion.* *2. Revise the feeding procedure of BPO as dissolve the BPO in the solvent before feeding to the reactor.* *3. Set the emergency SOP of BPO being unable to enter the reactor, and train the operators.* *4. Post the*

										precaution of "No knocking for BPO".
								☐	☐	
								☐	☐	
								☐	☐	
								☐	☐	
								☐	☐	

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