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Exposure Control and Process Safety
Of Monomers in Selected Plastics and Rubber Industries

by

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TABLE OF CONTENTS

ABSTRACT

A review of the literature of monomers was conducted that incorporates polymer science and contemporary toxicology and epidemiology studies associated with their exposures. This review, supplemented with a history of monomer exposure control technologies and protocols, helped establish the basis for a questionnaire created to ascertain and examine best practices in process safety. This questionnaire, in the form of interviews, open discussions, and detailed entries, was employed to identify common themes applicable for consensus guidelines in the chemical industry. Environmental Health and Safety (EHS) professionals, including safety engineers and industrial hygienists, were recruited from a range of chemical companies that use monomers to produce plastics and rubbers. Among the observations by these professionals was the recognition of professional discipline as a key motivator of EHS best practices, especially during routine evaluation and implementation of safety programs. Another main observation was the importance of advancing worker and contactor training, in tandem with the retention of highly qualified workers. Results of this study suggested that progress in EHS may be inhibited by redundancies in safety programs, challenges in achieving zero incident targets, and requirements for third-party stewardship programs. Additionally, the commercial availability and support of state-of-the-art engineering controls and cooperation of experts within professional and trade associations were found to be major drivers in process safety. It is therefore crucial that regulatory directives and standards concerning polymer production are reevaluated, updated, and repurposed to provide flexibility in achieving compliance and risk prioritization.

I. INTRODUCTION

The ability to harness polymers has enabled us to mass-produce some of the most versatile materials. During the World War II wartime economy, the demand for these materials, as rubbers and plastics, saw its largest historical increase. The production of synthetic rubber in the United States in particular was a key driver, as the Axis powers controlled nearly all the world's limited supplies of natural rubber by mid-1942. During this period of history, the U.S. Office of War Production began contracting with chemical companies to spur the development of polymer technologies (Gupta, 2018). Following this major shift, the manufacture of polymers became a dominating economic force. There are now approximately 680,000 plastics and rubber workers creating polymers in the United States alone (DOL Statistics, 2016), providing materials to us that are now essential for the modern lifestyle.

During this economic boom, there were many signs of a distressed workforce related to their exposure to monomers used in the production of polymer materials. "Rubbertown" in Louisville, Kentucky is a classic example of an industrial neighborhood now host to 11 large chemical facilities that have experienced a range of cancers and respiratory illnesses due to chemical exposures, many of which are related to polymer production. Rubbertown is just one example of a worldwide problem of various degrees of risks posed to plastics and rubber workers (WJCCTF, 2017) (Bruggers, 2017). There are significant risks of monomers to the health and safety of industrial workers through the induction of toxicity, cancer, and dermatitis. Monomers even play a significant role in industrial fires (International Agency for Research on Cancer, 2016). This research aims to develop the necessary EHS precautions for these workers with these risks in mind.

II. REVIEW OF THE LITERATURE

The goals of this literature review are to describe literature that relates to guidelines of exposure control and process safety within the polymer industries, and to identify priority chemicals in these industries that pose the most significant health risks to polymer workers. These literature review findings ultimately help to develop key EHS prevention and control strategies of polymers and how they, as a general class of chemicals, should be most effectively controlled for regulatory and scientific purposes. Following this literature review, research results are provided that identify critical control strategies. This research incorporates a questionnaire, submitted to polymer industry representatives, which aims to capture attributes of effective health and safety protocols.

Characteristics of Polymers

Polymers are chained networks of covalently-bonded monomer molecules that can be configured into a wide variety of structures. There are three distinct classes of polymers that are used and are differentiated by their “viscoelastic” properties: these include a material’s resistance to flow, and its degree of coiling. Crosslinking is often employed within polymers to create internal stability and increase viscosity. Coiling of polymers is used to produce elasticity which means that the material can be stretched and return to its resting state. The three classes of polymers are elastomers (e.g., polybutadiene rubbers), thermoset plastics (e.g., polyurethane) and thermoplastics (e.g., polyvinyl chloride) (American Chemistry Council, 2005).

Elastomers are heat resistant, elastic polymers that are composed of cross-linked networks of coiled polymers. The coiling of elastomers generates their high elasticity. This property of rubber is perfect for tires because they can absorb friction, shock, and heat. *Thermoset plastics* are rigid polymers that are cross-linked networks of non-coiled segments. Thermoset plastics are generally the most heat and chemical-resistant among polymers (American Chemistry Council, 2005). *Thermoplastics*, which comprise of a large majority of plastic products (92%), lack cross-linking. While thermoplastics are not as chemical and heat-stable as elastomers and thermoset plastics, it is that characteristic that gives them a major advantage. Thermoplastics can be readily molded and recycled, thus they are very economically viable (American Chemistry Council, 2005).

Polymers are unique among chemical intermediates in that they display a very broad range of physical properties and can form many kinds of materials such as fibers, sheets, foams, and intricate molds. Because of their versatility and advantageous properties such as chemical resistance, insulation from heat and electricity, and their light weight, polymers are widely used to create an expansive array of materials essential to the modern lifestyle (American Chemistry Council, 2005).

Types of Manufactured Polymers

Of the three classes of polymers, there are distinctly different kinds of potential configurations or “types” that are economically feasible. The largest class of polymers in industry is thermoplastics, followed by elastomers, and thermosetting plastics. The most widely produced “thermoplastic” is polyethylene (PE), which comprises about 30% of all plastics produced, and is used for packaging materials (e.g., plastic bags, films, and bottles) (PlasticsEurope, 2016).

Polypropylene (PP), at almost 20% of the thermoplastic market, includes folders and packaging caps. Another type of thermoplastic is polyvinyl chloride (PVC) (10% of the market), which is used in PVC pipes and flooring. Polystyrene (PS), polypropylene (PP), and polyethylene terephthalate (PET) comprise of the other widely produced thermoplastics. “Thermosetting” plastics include epoxies, polyesters, ureas, melamines, phenolics, and polyurethanes and are used in a variety of applications such as electrical insulators and car bodies (PlasticsEurope, 2016).

Among elastomers, some of the most widely produced materials are styrene-butadiene rubber (SBR), polybutadiene rubber (BR), isobutylene isoprene rubber (IIR), and polyisoprene rubber (IR) that are used in tires, door and windows, hoses, belts, matting, and flooring. There are many other elastomers used to create specialized construction and industrial products, such as ethylene-propylene rubber (EPR) and polychloroprene rubber (CR) (Siemens AG, 2013).

Polymer Industries

The rubber and plastics industries are combined into the same subsector, NAICS 326, as recognized by the U.S. Department of Labor, because rubber and plastic materials have related technical properties and similar constituents. In general, these industries specialize in one or a few polymers, with the major exception of tire manufacturing. The plastics and rubber industries comprise of 5.5% of the American workforce within the manufacturing sectors, totaling 680,000 American workers. Eighty percent of the 5.5% fraction is employed in the plastics industries, and 20% is in the rubber industries. China, Europe and the US, and the rest of Asia have the highest production of plastics, and Asia dominates the rubber market (BLS, 2016).

Polymer Processes – Polymerization and Manufacturing

Monomers used in the plastics and rubber industries are distilled from petroleum, coal, and natural gas, and are then sent to manufacturers that use them to create polymer products. After the addition of additives such as plasticizers and fire retardants to polymer products, they are then shipped to plastic manufacturers in the form of powders, liquids or pellets where they are transformed into a whole host of plastic products. There are several different methods used to form plastic resins into the final product. The main methods are injection molding, extrusion, blow molding, calendaring, and compression molding (DeMatteo, 2011).

Chemical Hazards in Polymer Industries and their Related Health Effects

This section describes the toxicology and epidemiology literature on monomers regarding their carcinogenic potential and, later, control strategies that help mitigate this potential. The findings were drawn from scientific articles (after 2006) that highlight research that aims to advance standards for these chemicals. While there are many governmental and industry publications that describe the comprehensive knowledge of these chemicals, this literature review focuses on a range of studies that aim to develop knowledge and standards even further.

The development of exposure control strategies arises from strong scientific evidence. Verma et al. (2002) suggested that toxicology, epidemiology, occupational medicine, occupational hygiene, and unions/workers play an integral role in developing process guidelines for various chemicals. Verma et al. (2002) recognized that toxicology has the role of establishing dose-response relationships, toxicity and disease mechanisms, and candidate biomarkers for biological monitoring, and that epidemiology has the role of establishing exposure-effect relationships and validating biomarkers for biological monitoring.

Formaldehyde

Formaldehyde is primarily used for plastic resin production such as urea-formaldehyde resins, phenolic resins, and epoxy and melamine resins. The International Agency for Research on Cancer (IARC) has classified formaldehyde as a Group 1 carcinogen (DeMatteo, 2011). It was found to be linked to an increase in breast cancer risk in a 1995 study of industrial workers (Cantor, 1995). Formaldehyde is released during thermal processing and is most likely present during overheating events such as machine malfunctions, purging or maintenance operations (DeMatteo, 2011).

Benzene

While benzene is now universally recognized as a human leukemogen, this was not the case 35 years ago even though the first report clearly associating benzene with leukemia was published as early as 1928. However, the causal evidence did not prompt new control strategies. In fact, major improvements in workplace control of exposure to benzene were not made until the 1970s. Before that, the control strategy was based on benzene's anesthetic effect. As the exposure limit was gradually reduced, there was a need at the workplace for new methods of biological monitoring. As a result, determination of S-phenylmercapturic acid and t,t-muconic acid in urine have now replaced the "phenol" biomarker in urine because the original method lacked the necessary sensitivity when exposures were less than about 5 ppm (Verma et al., 2002).

Vinyl Chloride

Vinyl chloride is the basis of polyvinyl chloride (PVC) resins for the manufacture of pipes, tubing, fabrics, and auto parts. Vinyl chloride can be released during resin production and thermal processing. It is an IARC Group 1 carcinogen (DeMatteo, 2011). The danger of vinyl chloride exposure is best demonstrated by its induction of cancer, through the angiosarcoma of the liver (ASL). The first hallmark study establishing the undeniable connection of vinyl chloride exposure to human carcinogenicity was in the published cases of ASL among men employed in the manufacture of PVC resins by BF Goodrich in 1974 (Infante et al., 2009). This finding was a turning point for vinyl chloride exposure control and was the necessary catalyst for OSHA in issuing a Final Rule for vinyl chloride that effectively lowered the Permissible Exposure Limit (PEL) to 1 ppm (Infante et al., 2009).

ASL epidemiological studies found that workers exposed to vinyl chloride were receiving ASL at 10,000 times the rate of the general population. Given that there is an extreme rarity of

ASL in the general population, IARC concluded that the association between the exposure of industrial workers to vinyl chloride monomer and the induction of ASL is evidence of a causal relationship (Grosse et al., 2007). Prior to 1974, epidemiological studies and case reports demonstrated vinyl chloride's association with angiosarcoma of multiple tissues, hepatocellular carcinoma (HCC), neoplasms of connective and soft tissue, and lung and brain cancer (Grosse et al., 2007).

In 1974, OSHA issued an Emergency Temporary Standard (ETS) to reduce the acceptable vinyl chloride exposure limit from 500 ppm to 50 ppm, and later in the same year, OSHA promulgated a final standard to reduce the PEL to 1 ppm (TWA) and 5 ppm (STEL) (Infante et al., 2009). It also contained supplementary provisions, including exposure monitoring and medical surveillance requirements. Following this standard, the Consumer Product Safety Commission (CPSC), the Food and Drug Administration (FDA) and the U.S. Environmental Protection Agency (EPA) took steps in 1974 to remove consumer products with vinyl chloride from the marketplace and, through legal battles, were able to ban or recall vinyl chloride-containing products in aerosols such as insecticides, paint sprays, and hair spray products (Infante et al., 2009).

Vinyl chloride's potential to induce carcinogenicity has been well documented and researched. It is understood that the vinyl chloride metabolite, chloroacetaldehyde, binds to DNA because it has strong "electrophilic" properties, and these binding "adducts" can cause mutations. Various toxicology studies have proposed the mechanism of carcinogenity of vinyl chloride is through the reaction between chloroacetaldehyde and guanine, giving rise to 7-(2-oxyethyl)guanine) (Bren et al., 2006). These toxicology studies have also been essential in developing biomarkers that should be used in industry as part of necessary medical surveillance of vinyl chloride (Chang et al., 2015).

Toxicological studies have identified useful biomarkers of exposure, effect, and susceptibility to vinyl chloride, and provide the molecular basis for prevention and treatment of vinyl chloride cancers. Not only do these studies enable proper monitoring of the carcinogenic process, it also can help develop treatments for various medical conditions. Based on the evidence, certain blood serum biomarkers (i.e., mutant ras-p21 and mutant p53) accurately reflect the occurrence of mutational changes in tissues, occurring in a dose-response relationship (Brandt-Rauf et al., 2012).

Many methods are used for biological monitoring of workers for vinyl chloride. Exhaled breath is one sample type that can be used to study biomarkers. In one study (Azari et al., 2016), a total of 100 workers and 25 control subjects from two plastic manufacturing plants in Tehran, Iran were studied. NIOSH method no.1007 was used to analyze Tedlar® bag samples that contained exhaled breath from workers of exposed and controlled groups and employed GC-FID for analysis. Findings from this study showed that the mean occupational exposure of workers to vinyl chloride monomer in one of two plants was higher than the respective threshold limit value (TLV). The authors recommended that Tedlar® bags be used as they are more practical, less complex and less expensive than blood sampling, and provide a more accurate quantitative estimate of exposure than blood analysis and DNA adduct analysis (Azari et al., 2016).

Abdel-Rasoul et al. (2016) found that exposure to high levels of vinyl chloride and styrene is implicated in the increase in frequency of chest manifestations (rhinitis, cough, expectoration and dyspnea) and early spirometric changes (obstructive ventilator function). Recommendations included the use of an automated plastic grinding machine to decrease the exposure to dust, appropriate personal protective equipment (PPE), and spirometry in pre-employment and periodic medical examinations (Abdel-Rasoul et al., 2016).

Styrene

Styrene is an aromatic hydrocarbon, naturally occurring in gummy exudates from the trunks of certain trees. Styrene is used in the production of various plastics, resins, and vulcanizers such a styrene butadiene rubber, acrylonitrile-butadiene-styrene (ABS), and styrene-acrylonitrile resins. It is considered an endocrine disrupting compound (EDC) and is a Group 2B carcinogen (DeMatteo, 2011).

One toxicological study detected the presence of the styrene in male workers of plastic factories in Egypt, demonstrated common health effects of styrene exposure by laboratory investigation, and correlated the duration of styrene exposure and its level in the blood with the severity of health effects (Helal & Elshafy, 2012). The methodology included a medical exam, ventilator function tests, and analyses of biomarkers of styrene: B2 microglobulin in blood, urinary mandelic acid in urine, and styrene in blood. The study recommended the implementation of pre-employment and periodic medical examinations and health education programs using PPE and following the recommended exposure limits (Helal & Elshafy, 2012). A statistically significant correlation was found between the duration of styrene exposure and ventilator function parameters, and between the duration of styrene exposure and detectable chromosomal aberrations (Helal & Elshafy, 2012).

Ethylene Oxide

Ethylene oxide is a monomer that is widely used as a chemical intermediate in many industries and most human exposure occurs from its use in sterilization medical equipment. Ethylene oxide exposure is affiliated with an increase incidence of tumors of the lung, Harderian gland, lymphomas, uterine adenocarcinomas, and mammary carcinomas, mononuclear-cell leukemia, brain tumors, peritoneal mesotheliomas of the testis, and subcutaneous fibromas (Grosse et al., 2007).

A key epidemiological study (Gross et al., 2007) of industrial facilities where ethylene oxide was used was conducted, and the study benefited from a low potential for confounding by concomitant exposure to other chemicals. The study found an association between cumulative exposure and mortality from lymphoid tumors, which include non-Hodgkin lymphoma, multiple myeloma, and chronic lymphocytic leukemia. One internal analysis of 7,500 women showed a significant relationship between ethylene-oxide exposure and breast-cancer incidence, with the risk doubled among women with higher cumulative exposures (Grosse et al., 2007).

Ethylene oxide is classified as a Group 1 carcinogen and is an alkylating agent that directly reacts with DNA. It is a mutagen and clastogen at all phylogenetic levels, and induces heritable translocations, sister chromatic exchange, chromosomal aberrations, and micronucleus formation in the lymphocytes of exposed workers (DeMatteo, 2011). Mikoczy et al. (2011) found that exposures to ethylene oxide at 0.13 ppm-years in a cohort of Swedish sterilant workers employed for at least one year did not show a statistical increase in lymphohematopoietic tumors. However, when only female workers were analyzed, with a cumulative ethylene oxide exposure increase, the incidence of breast cancer increased significantly (Mikoczy et al., 2011).

Butadiene

1,3-butadiene is mainly used in the production of synthetic rubbers. Workplace concentrations in the United States, Canada, and Western Europe, are generally below 2 mg/m^3, but can be higher in countries that use older technologies (Grosse et al., 2007). Inhalation studies have shown increased incidences of lymphoma and neoplasms. Toxicological studies show that butadiene induces DNA adducts, micronuclei aberrations, and chromosomal aberrations in human lymphocytes. Epidemiological studies show an increased risk of mortality from chronic lymphocytic and myelogenous leukemia, especially among those hired before and during the 1950s when hot-production of BSR rubber was produced (Grosse et al., 2007).

Priority Chemicals in the Polymer Industries

This literature review aims to establish priority chemicals in the polymer industries that carry the most significant risks to worker health and safety. Monomers deserve attention, not only because they are unique among chemical intermediates used in the manufacturing sector, but also because they have significant biological and physical hazards, including carcinogenic potential, flammability, toxicity, and irritation to skin and eyes.

Lithner et al. (2011) produced a list of 55 plastic polymers and their associated monomers and co-monomers and made a ranking of the polymers that have the highest health hazard risk, wherein a classification system called Annex VI of the EU CLP was adopted to organize chemicals into hazard classes ranging from I to V. The hazard classes sorted as level V were: carcinogens (class 1), mutagens (class 1), and reproductive toxicants (class 1). Those sorted as level IV were mutagen (class 2), acute toxicants (class 1 & 2), respiratory/skin sensitizers, and specific target organ toxicants (Lithner et al., 2011). The most frequent hazard classifications were skin sensitization (class 1), respiratory irritation (class 1), acute toxicity (class 3), serious eye irritation (class 2), and carcinogenicity (class 1A & 1B). Of these 55 monomers, 31 had a health ranking of IV or V. Of these 31 monomers, 23 are suspected or known carcinogens according to the National Toxicology Program (NTP) or the International Agency for Research on Cancer (IARC). Lithner et al. (2011) also created a scoring system to further rank the monomers. For each of the 5 hazard levels, grades increased by a factor of 10 for each level, carcinogenicity being at the highest hazard level. According to this classification system, polyurethanes, PAN, PVC, epoxy, and styrenic copolymers ranked as most hazardous (Lithner et al., 2011).

The International Agency for Research on Cancer (IARC), the National Toxicology Program (NTP), and the US EPA provide many toxicological and epidemiological assessments that help determine the priority and rank of these chemicals (DeMatteo, 2011). The chemicals used in the polymer industries that are identified carcinogens (by the IARC and NTP) are:

> acrylamide, acrylonitrile, benzene, 1,3-butadiene, chloroprene, 1,4-dichlorobenzene, epichlorohydrin, ethylene oxide, formaldehyde, isoprene, 4-4’-methylenedianinline, propylene oxide, styrene, styrene-7,8-oxide, tetrafluoroethylene, vinyl chloride, toluene diisocyanate, urethane, and vinyl chloride

(International Agency for Research on Cancer, 2016) (National Toxicology Program, 2016).

Scientific Advancements in Exposure Prevention and Control

Various workplace prevention strategies include engineering controls such as ventilation (e.g., fixed hoods for soldering benches, moveable hoods and ducts), process isolation (e.g., enclosure using a closed vat or closed-loop system), process modifications, and process automation (Verma et al., 2002). Other prevention strategies include using substitutions with less hazardous substances, adopting appropriate PPE, and implementing work practice changes, education and training, and surveillance. Surveillance activities include exposure monitoring, and biological monitoring. Breaking down exposure assessments by job tasks can be applied, such as employing Job Hazard Analysis (JHA) or a Job-Exposure Matrix (JEM) by different polymer processes: resin preparation, molding machine operations, molding processes, finishing, fabricating, paint and decorating, plastic recycling, and purging/cleaning operations (Verma et al., 2002).

According to DeMatteo et al. 2012, a general overview of worker exposures to monomers could be better established. There are a few studies that do aim to characterize exposure in the plastics and rubber industries. DeMatteo et al. (2012) included interviews of unionized employees in plastics industries about working conditions, job tasks, plant layout, chemicals used, protective controls, historical changes, exposure concerns, improvements needed, and most importantly, perceived barriers to gaining improvements. While major technological advances have been made in resin polymerization, which effectively contain fugitive emissions, findings outline a general need for proper ventilation in secondary operations. There is also an opinion among workers of possible deception occurring in audits, masking real exposure levels (DeMatteo et al., 2012).

According to biomonitoring studies, concentrations of monomers in blood and urine of exposed workers are at levels 5 to 10 times higher than the non-exposed workers within the same industry, and the degree of materials handling is a good predictor of positive biomarkers. Findings showed the existence of an excess risk of male breast cancer among workers in these industries, and a double in the odds of women getting breast cancer being linked to exposure to various endocrine disrupting chemicals (DeMatteo et al., 2012). Another striking finding is an increased risk of spontaneous abortions, delayed conception, premature delivery, and congenital malformations in the offspring of women rubber workers (DeMatteo et al., 2012).

Neves et al. (2006) studied a cohort of male workers to investigate cancer deaths according to company size. When compared to employees of larger companies, workers employed in small companies showed a greater risk of death due to any type of cancer. Risk of death was greater among workers employed in production, shipping, and maintenance (Neves et al., 2006).

Brophy et al. (2012) found across all sectors that women in jobs with high exposures to carcinogens had an elevated cancer risk, with automotive plastics manufacturing as a specific sector having the highest elevated risk. Premenopausal breast cancer risk was highest for automotive plastics, while a quadrupling of breast cancer risk was found among male workers in the rubber and plastics industries (Brophy, 2012). Labrèche et al. (2009) recently found an excess risk of breast cancer for occupational exposure to acrylic fibers.

Technological Advances in Monomer Exposure Reduction

Worker exposure levels to monomers had its largest decline in 1974, following the adoption of OSHA regulations concerning vinyl chloride, which was one of the first industrial chemicals regulated by OSHA. The control and prevention strategies that emerged through regulating vinyl chloride consequently reduced exposures to many different monomers. The chemical company, BF Goodrich, was a pioneer in producing new engineering designs post-1974 (US EPA, 1978). These strategies include automating processes that enabled a large reduction in exposure to "manual vessel cleaning," a work activity that was the most contributing factor in the development of occupational cancers. Vessel cleaning, an activity when workers got into polymerization tanks to scrape residue, was typical of pre-1974 polymer workers. Other important strategies that resulted following the 1974 OSHA regulations include reducing work forces, improving reactor cleaning methods, using larger reactors, improving stripping operations, and installing more control equipment. As part of the automated cleaning process of reactors, high pressure water or solvent began to be used and "clean wall" materials that coat the vessel walls were used to prevent the polymer from sticking. Additionally, the use of large reactors is considered an important advancement since they have fewer connections and therefore fewer potential leaks and require less manual cleaning. The process of stripping is also essential to control emissions. Manufacturers began to phase out grades of resin which are difficult to strip well. Because of all these changes in the engineering controls, PVC plant exposures now average between 1 and 3 ppm (US EPA, 1978).

Prior to 1974, there were technological changes that may have increased occupational cancers. According to task-specific exposure estimates of the butadiene-styrene industry made by Macaluso et al. (2010), changes in exposure levels to butadiene and styrene was marked by the introduction of cold polymerization in the 1950s. While this reduced exposure to fugitive emissions from chemical operations, because of less heat applied to the process, cold polymerization consequently increased the frequency of "manual vessel cleaning" because the polymer residue would accumulate under less heat. Exposure to butadiene and styrene did decline sharply in the 1970s and 1980s following the 1974 OSHA regulations with the implementation of automated reactor cleaning and stripping of residues that reduced "manual vessel cleaning." Also, during this period, hydroblasting techniques were introduced that shortened the time of exposure and there was a shift to outsources equipment cleaning to contractors (Maculso et al., 2010).

Yet, much technological advancement that improved monomer exposures did occur without OSHA involvement. For example, some of the significant changes in engineering designs for butadiene and styrene production occurred decades before the OSHA regulations for butadiene in 1997. Worker exposure to monomers occurred following technology changes from high-loss reciprocating pumps with packaging during the 1940s-1950s, to centrifugal pumps with single mechanical seals during the 1950s-1970s, to the present technology based on double mechanical seals or seal-less pumps (Maculoso et al., 2012).

Thermal Runaway Incidents in Polymer Industries

Polymerization plants carry the risk of using flammable materials and unstable reactions that have produced major industrial fires and calamities and have proven to be the most common type of manufacturing plant that produces fires. Vinyl chloride and ethylene oxide are responsible for some of the largest fires. Runaway reaction incidents from the most recent 25 years (1988-2013) have been studied (Saada et al., 2015). Most of these reported incidents occurred in polymerization and decomposition processes. This study aimed to determine causes of thermal runaway incidents and compare those reported in pre-1988 and post-1987. It was found that operator error and management failure contributed to 50% of the runaway incidents, and lack of operating procedures was another major contributor. The number of fatalities and injuries following thermal runaway incidents post-1987 increased by about 300% as compared to pre-1988, even though the number of incidents had lowered dramatically from 189 incidents to 30 incidents during these periods (Saada et al., 2015). Incidents were found to occur due to a basic lack of proper understanding of the process chemistry and thermochemistry, inadequate engineering design for heat transfer, inadequate control systems and safety back-up systems (e.g., venting), and inadequate operational procedures (e.g., training) (Saada et al., 2015).

According to Saada et al., 2015, a formal process hazard analysis (PHA) system should be used to identify hazards, determine how likely they are to occur, and how serious the consequences could become. Some of the necessary information related to process chemistry is modelling of reactions (Saada et al., 2015). The identified causes of thermal runaway incidents were: little or no study or research and development (R&D) work being done before scaling up and going into production (18%); mischarging of reactants which include overcharging, wrong material, too rapid addition, wrong sequence, undercharging, and improper controls (32%); temperature control failures (9%); presence of impurities, e.g., water, in raw materials (11%); maintenance–related causes (11%); and operations failure to follow written instructions (5%). Of the chemical processes involved, polymerization accounted for 17 incidents. The polymerization reactions involved in these incidents include vinyl chloride (9 incidents), polyester resin (2 incidents), vinyl acetate, butadiene/acrylonitrile, hydroxyethyl methacrylate, and urea-formaldehyde (due to contamination of the urea with ammonium nitrate) (Saada et al., 2015).

An accident case study by Bhattacharjee et al. (2014) was conducted regarding a process of phenol-formaldehyde production, which used ammonia as a catalyst in a new trial run. Due to an operator’s mistake, nitric acid was added to the reactor instead of ammonia as a catalyst, and a runaway reaction was initiated. Job Hazard Analysis (JHA) and SWOT analysis found that the major lessons learned is that all reactants should be labelled properly and kept in the proper place in storage. SWOT Analysis helps identify Strengths, Weaknesses, Opportunities, and Threats. An adequate cooling arrangement should also have been provided to the reactor. Other essential duties are training, preparation of standard operating procedures (SOPs), and use of a proper-sized relief valve (Bhattacharjee et al., 2014).

According to the U.S. Chemical Safety and Hazard Investigation Board (CSB), in February 2003, an incident occurred as part of a PVC polymerization process. An operator at a Formosa plant in Baton Rouge, Louisiana opened the bottom valve on the wrong reactor. Some safety improvements were made in Baton Rouge, but the company determined that changes were not needed in Illiopolis where another incident would occur in 2004 because the valve controls were different (Ness, 2015).

On April 23, 2004, five workers were killed, and two others were seriously injured when an explosion occurred in a polyvinyl chloride (PVC) production unit at the Formosa Plastics plant in Illiopolis, Illinois (Ness, 2015). The Chemical Safety Board (CBS) found that the accident occurred when an operator overrode a critical valve safety interlock on a pressurized vessel making PVC. Vinyl chloride liquid and vapor was discharged into the plant and was ignited, resulting in a massive explosion (Ness, 2015). Additional safeguards, such as locks to secure the interlock system, could have prevented the critical valves from being opened when the reactor was pressurized. No gauges, indicators or warning lights were present to inform operators on the lower level of the reactor's operating status.

Years later, in 2016, at the Pemex vinyl chloride plant in Coatzacoalcos, Mexico, another vinyl chloride explosion occurred, killing 36 people and injuring over a hundred. Because of the hazards of vinyl chloride, it is usually stored in double-walled containers under pressure, with leak monitors that detect low levels of leakage from the inner container before the outer wall in breached. No explanation came from this disaster and it can be interpreted that the leak monitors malfunctioned (Tullo, 2016).

Priority List of Chemicals for the Study

In the literature review, a list of priority chemicals in the polymer industries was established. Chemicals selected for the *Priority List* below were chosen from a list of carcinogens recognized in the polymer industries via the National Toxicology Program (NTP), the International Agency for Research on Cancer (IARC), and the US EPA, and specifically among those that are major commodity chemicals, with over 10 million tons in global annual production.

The priority list of six chemicals developed here in focus for this thesis includes**:** formaldehyde (52 million tons), benzene (51 million tons), vinyl chloride (40 million tons), styrene (26.4 million tons), ethylene oxide (24.2 million tons), and butadiene (12.7 million tons).

Four of these chemicals appear in the OSHA Z-Tables: benzene, formaldehyde, vinyl chloride, and ethylene oxide. Five of these chemicals have an IARC carcinogenic rank of 1 (i.e., the highest rank of carcinogen plausibility): vinyl chloride, benzene, formaldehyde, and ethylene oxide. These results suggest that it is commodity chemicals that generally allure the most research and regulatory oversight.

There are many lesser known chemicals that may be good candidates for these lists, specifically, there are many analogous, chemically-derivative, and metabolite chemicals that could be added. Styrene, benzene, toluene, and phenols, for example, have similar chemistries and could be grouped for regulatory purposes if research clarified the extent of their similarities and their mechanisms of action (MOAs). Some chemicals (e.g., vinyl acetate) that have weaker evidence of contribution to various human health risks could be better clarified through this type of comparative analysis. According to observations made through the literature review, many monomers produce DNA adducts through methylation and those of which produce epoxide metabolites tend to produce mutagenic effects that produces carcinogenity (e.g., 1,3-butadiene, and vinyl chloride), while quinone metabolites tend to be produce epigenetic effects that enable carcinogenity (e.g., styrene and benzene) (Guengerich, 2000).

III. SPECIFIC AIMS OF THE STUDY

The main purpose of this study is to assess the current best practices in the rubber and plastics industries related to exposure control and process safety.

The specific objectives for this study are to:

1. Establish representative chemicals in this study, including formaldehyde, benzene, vinyl chloride, styrene, ethylene oxide, and butadiene.
2. Characterize and rank the implementation of control measures to reduce rubber and plastics worker chemical exposures.

3. Assess challenges in achieving progress in EH&S programs.
4. Assess the advancement of standard operating procedures (SOPs) and training to reduce exposures.
5. Review the application of Product Stewardship Guidelines associated with each priority chemical (identified in #1 above).

IV. RESEARCH QUESTIONS

The research questions for this study include:

1. What are the representative priority chemicals that can be established for the polymer industry?
2. What are the preventive measures implemented in the rubber and plastics industry to reduce worker exposure to these chemicals?
3. How are Product Stewardship Guidelines (PSG) being applied and/or reviewed in implementing site-wide EHS policies related to exposure control and process safety?
4. What are the major challenges to implementing and improving health and safety plans in rubber and plastics manufacturing facilities?
5. What are the best practices for the rubber and plastics manufacturing facilities that have made significant progress for worker protection against chemical exposures?

V. SIGNIFICANCE OF THE STUDY

This study aims to contribute to the body of knowledge of current best practices related to exposure control, process safety, and risk management concerning industrial monomers. This study also is designed to investigate the application of health and safety efforts, programs, and activities that aim to monitor or reduce exposures to industrial monomers to progress those best practices in the rubber and plastics industries.

Specific contributions would be to the target audience: Environmental Health and Safety (EHS) Professionals such as EHS Managers, EHS Specialists, Industrial Hygienists, and Chemical Engineers in the rubber and plastics industries as well as industrial researchers, consultants, and

OSHA and NIOSH government officials, who could apply the concepts found within this study to develop policy, specify in writing, and implement health and safety programs to reduce exposures to selected chemicals.

The significance of the study is to help EHS Professionals fine-tune their efforts, time, and funds to exposure prevention and risk management as it relates to industrial monomers in the plastics and rubber industries. Because controlling cancer-causing agents requires a high level of organization, many integrated and disciplined strategies must be applied company-wide. Results will also provide a genuine assessment of the current needs and hurdles related to exposure monitoring and minimizing industrial monomer exposures.

VI. METHODOLOGY

This study was initially proposed to utilize a cross-sectional design to collect data related to the implementation of exposure control and process safety at rubber and plastic manufacturing facilities throughout North and South Carolina. However, throughout the course of the recruitment process, there were significant challenges in recruiting enough participants necessary to ascertain trends and statistics. A target of recruiting 12-15 professionals was originally set for the study; however, the recruitment fell short of meeting that target. While a total of 20 professionals acknowledged the invitation to participate, only 5 professionals provided a response. Since the sample size was not sufficient to conduct a quantitative analysis, alternatively, a qualitative analysis was completed that explored general themes.

Participant Selection and Recruitment

A sample of rubber and plastic facilities was selected for recruitment of participants using data from the Toxics Release Inventory (TRI) and NAICS codes, as well as industry or marketing databases, and general searches. The potential participants were chosen based on the following selection criteria:

1. The rubber or plastic facility is in North Carolina or South Carolina.

   Note: Following difficulties in recruiting enough participants, the recruitment scope was broadened to the entire United States. This criterion of locality was originally convenient in setting up face-to-face interviews with industry representatives.
2. The industrial facility was either involved in the production of raw materials or intermediates, its transport, or its use in final production of plastic or rubber resins and products.

Another major goal in the data collection strategy was recruiting participants that incorporated a variety of workers and industry representatives who work with industrial monomers. These workers included EHS professionals (managers or specialists), chemical/process engineers, or staffed industrial hygienists at a rubber, plastic, or related facility.

The actual number of interviews to be conducted was largely dependent on the response rate and not on the time of completion. One of the original goals of this research was to obtain approximately 12-15 questionnaire recruits similar to a methodology reviewed (Jones, 2013). According to this methodology, receiving 7-9 responses at a 15% response rate was relatively achievable, and it was posited that 20 responses at a 50% response rate could be potentially achieved (Jones, 2013). Approximately 100 individuals were contacted, and of those individuals, 20 responded of which 5 agreed to participate in the study. The resulting participation response rate was 5%, which was significantly lower than the anticipated conservative response rate of 15%.

The first collection source to find participants was from the Toxics Release Inventory (TRI) and the Chemical Data Reporting (CDR) databases from the U.S. Environmental Protection Agency (US EPA) website. Under the Toxic Substances Control Act (TSCA), EPA requires private industries to report releases, imports, and exports of hazardous chemicals. These databases provide an indirect method for finding potential participants. The EPA TRI Explorer Tool was used to search for a call list. Facilities were searched by priority chemicals that they produce including formaldehyde, styrene, butadiene, vinyl chloride, ethylene oxide, and benzene. According to the TRI inventory, there are hundreds of facilities registered by each priority chemical specified earlier in this report (Table 1).

Table 1: Number of Facilities Producing Priority Chemicals by State*

Chemical Produced	North Carolina	South Carolina	Virginia	Georgia	Tennessee	Number of Facilities TRI Registered
Formaldehyde	9	10	2	8	1	727
Ethylene Oxide	4	6	3	5	2	118
Vinyl Chloride	1	0	0	0	0	40
Benzene	2	3	3	1	1	915
Styrene	4	4	2	2	4	1168
Butadiene	2	0	1	0	4	198

* TRI Explorer (@https://iaspub.epa.gov/triexplorer/tri_release.chemical)

Another goal in the recruitment process was to incorporate professionals that work with each of the priority chemicals established. The final research participant list achieved representation of four of the six chemicals on the priority list, including vinyl chloride, benzene, styrene, and butadiene. Lastly, another goal created in the recruitment process was to concentrate on facilities located in North Carolina and South Carolina. Due to a low participation rate, the geographical scope of the participant recruitment was broadened. Alternatively, participants were recruited from the Table 1 full list, which includes facilities located throughout the entire United States. Approximately 150 facilities were called, including Table 1 facilities and additional facilities established through company clients. Among facilities producing butadiene and vinyl chloride, in particular, there was a lack of regional representation (i.e., from North and South Carolina) on the Table 1 list so facilities in Texas and Louisiana were also contacted.

Communication Prompt

All potential participants were informed that their participation is voluntary, that they have the right to stop participating at any time for any reason, and that their decision to participate or not participate would not involve any kind of penalty. Informed consent was obtained from all participants. See Appendices B and C for the scripts that were used to communicate throughout the recruitment process.

Challenges in Participant Recruitment

The most success in participant recruitment resulted from timely voice messages and emails, where a relatable story was crafted, and where appropriate follow-up messages were made. Participant recruitment, however, came with several challenges. As per the established methodology, safety professionals were contacted that had a visible public profile at a broad range of companies. An IRB-approved script (See Appendix B and C) was distributed by emails and voice messages that provided assurances of confidentiality, ease of contribution, and the significance of the research. However, no method of cold calling produced any significant results.

Through recommendations from a colleague, directors of several preeminent safety and health professional organizations were contacted. Through several channels of communication for months of follow-up, some directors were unreachable. Other directors exerted significant amount of effort into helping with the participant recruitment. These directors and other study participants sent recruitment email scripts to approximately 60 individuals involved in committees and professional groups. Unfortunately, no additional responses were received. It is assumed that the lower response rate during the recruitment process was because professionals were contacted that are employed in private industries, who frequently receive surveys by email, and who hold confidential or sensitive information about their industrial processes that are usually not readily disclosed.

Data Collection and Analysis

The approval (UMCIRB #17-002908) from the Institutional Review Board (IRB) of East Carolina University (ECU) was obtained prior to any data collection. A goal of fifteen comprehensive face-to-face or telephone interviews was made to be conducted with rubber and plastic industry representatives. There were no telephone interviews, as participants preferred a more formal setting. One face-to-face interview lasted for approximately one hour, during which the participant was asked to respond to questions about the implementation of EHS initiatives, such as engineering controls, adaptations and planning for industrial process changes, team integration of industry specialists and managers, and proper engineering and chemistry evaluations and design, ventilation and safety systems, and training and monitoring of employees and work environments.

The survey instrument (see Appendix A) was derived from a qualitative study conducted by the University of Winsor in collaboration with the National Network on Environments and Women's Health (DeMatteo et al., 2012). The interview/survey instrument was a combination of open-ended, yes/no type, multiple choice type and Likert-scale type (i.e., not applicable to strongly agree) questions. Open-ended questions were analyzed using the *common answers,* and Likert-scale questions were analyzed using *yes/no type answers*.

Interviews were transcribed to ensure accuracy and context of recorded responses. Interview transcripts were reviewed and all identifying information was removed to protect the anonymity of participants. The data collected from participants was encoded using statistical software called Qualtrics®. This program was used to interpret frequently cited hurdles in progressing health and safety plans in these industries, and where successful programs or preventive measures that reduce or mitigate exposures to industrial monomers have been implemented. Data was analyzed to identify key theme related to how and why preventative safety activities were implemented. The qualitative data collected was used to evaluate best practices of exposure control and process safety in these associated industries.

VII. RESULTS

Participant Description

Five participants were included in this study, all of whom contributed valuable responses. The participants provided three ways to provide responses: interview (n=1), questionnaire (n=2) and commentary (n=2). The interview was conducted face-to-face for approximately one hour and was highly productive as responses with a high level of detail were obtained. The questionnaires and commentaries were gathered through Qualtrics® and email submissions.

The original recruitment method consisted of making connections with safety professionals within different professions of EH&S and chemical industry backgrounds, in order to provide the best representation of the polymer industries. Among the study participants, there were two active process safety engineers and three expert consultants that had previous experience as process safety engineers. Of these participants, there was approximately 150 years of combined experience, with an average of almost 30 years of safety and health experience in the chemical industry, with a range of 15 to 40 years in the chemical industry. All participants had an engineering degree, including two with a PhD in industrial engineering, and each had a strong value of higher education, training, consultancy, and professional association affiliation. One participant was a published author on process safety, and another held four patents in engineering technology.

Participants worked at six major chemical companies in North Carolina and throughout the United States. Due to anonymity, the location or state of business was not disclosed. Participant recruitment utilized associations with colleagues as well as through professional networks, including the American Institute of Chemical Engineers (AICHE), the Center for Chemical Process Safety (CCPS), the American Society of Safety Professionals (ASSP), the Plastics Industry Association (PLASTICS), the American Industrial Hygiene Association (AIHA), and the Society of Chemical Manufacturers and Affiliates (SOCMA).

In the following sections, qualitative results are described and are organized by the original research questions established in the literature review section. The questions include the representation of the priority monomers, the best practices and preventative measures for chemical exposure reduction, major exposure control implementation challenges, and the application of product stewardship guidelines. Refer to raw results of the study from participant entries in Appendix D.

Represented Priority Chemicals of the Polymer Industry

Among the chemical priority list identified for this study, the chemicals used in the facilities of the study participants are vinyl fluoride (analogous to vinyl chloride), butadiene, styrene, and acrylics. Specifically, one participant identified using vinyl fluoride in their chemical process. The remaining four participants identified using butadiene, styrene, and acrylics in their production process. The chemicals identified through this study represent a good variety of monomer types, and all these chemicals were represented in their gaseous form, specifically as chemical intermediates for polymer production.

Best Practices for Chemical Exposure Reduction

Results showed that the following activities were among the most significant sources of progress in exposure control as identified by the research participants:

1) The development of training for workers, contractors, and vendors
2) The retention of valuable workers
3) The consistent application of internal and external safety audits
4) The adoption of self-policing guidelines (e.g., SafeStart®)
5) The implementation and review of safety programs and procedures (Plan, Do, Check, Act)
6) The application of the "hierarchy of controls" in exposure control activities
7) The "operational discipline" of safety professionals

Among the most important safety programs and protocols identified included:

1) Standard Operating Procedures (SOPs)
2) Managements of Change (MOCs)
3) Risk Management Plans (RMPs)
4) Permit to Work (PTWs)
5) Emergency Response (ER) Protocols
6) Job Safety Analyses (JSAs)

In reference to the Likert-scale questions, safety management activities are performed at different frequencies among the facilities represented. For example, the Process Hazard Analysis (PHA) team review was done monthly as reported by one participant and another participant reported that a team review was done every five years. Engineering evaluations for one participant was conducted every six months to five years, and another participant reported evaluation was conducted every three to five years. Overall, on a routine basis of less than six months, PPE was purchased. Engineering controls were purchased every six months to one year. Ventilation evaluations were performed monthly, and industrial hygiene surveys were requested routinely, less than every six months. Chemical process evaluations were conducted weekly. No differences in the frequencies were reported with respect to routine and non-routine chemical processes.

Major Challenges in Health and Safety Plan Implementation and Improvement

Major challenges to the implementation and improvement of plans were identified by participants. Among the most noteworthy comments was that “an improvement industry-wide could be achieved by reducing ‘parallel or duplicate programs,’ assessing ever-increasing challenges of achieving zero-incident targets, and effectively managing stewardship of third-party safety programs.”

The most demonstrable application of exposure reduction identified was investments towards installing state-of-the-art engineering controls, but according to the participant, the potential of that pursuit lies within commercial availability and support. The biggest challenge to process safety and exposure control identified was retaining and adapting to the loss of highly experienced personnel. According to one participant, on average, “it realistically takes about two years to adequately train up polymer workers, and the retirement or transfer of personnel with 35-40 year of experience means that many decades of experience among the facility personnel is lost in the process.”

Application and Review of Product Stewardship Guidelines

Results showed that Product Stewardship Guidelines are being referenced during Process Safety Management (PSM) step reviews. The role of process safety in this process was vital to the questionnaire participants. In fact, several of the participants actively taught concepts of process safety as an expert consultant. According to the participants, developing an awareness of process safety principles was invaluable.

Preventive Measures for Worker Exposure Reduction

While the hierarchy of controls was an established and well-accepted principle among participants, and while there were certain capital investments that were actively being considered that could reduce chemical exposure through new engineering designs, the viability and feasibility of these projects, however, required reliable commercial support. Many capital investments had successfully been implemented, and repair and maintenance of process equipment provided significant success in exposure reduction. New chemical processes were being evaluated consistently for worker chemical exposures. Assessing proper ventilation and respirators for workers as well as the adequacy of training were appropriate measures following the implementation of new chemical processes.

VIII. DISCUSSION

Findings from Questionnaire

Best Practices for Chemical Exposure Reduction Among Workers

Among the participant entries, there were several reoccurring themes. One important concept that was used by every single participant was the “hierarchy of controls.” It was well understood that the process and engineering applications of material containment, ventilation, and isolation are primary activities in exposure reduction, followed secondarily by administrative controls and PPE. Another recurring theme was the importance of safety training in achieving better outcomes, including contractor, employee, and vendor safety training. The review, auditing, and implementation of safety programs that follow established guidance documents was also a common response (e.g., SafeWork® Permitting, Process Safety Management (PSM), and Standard Operating Procedures (SOPs)). These reviews were understood by the participants to be ideally conducted by various divisions in labor, including supervisors, operators, technicians, and managers. No safety program mentioned was reviewed less frequently than one year. Additionally, it was mentioned that the safety culture and leadership drives the systems used to manage both the engineering and administrative controls to keep everyone safe from toxic exposures (i.e., operational discipline).

A few differences in the approaches of the participants were observed. One participant stressed the importance of auditing and training while another stressed the idea of "operational discipline." Another participant was alluding to the systemic application of the Deming Cycle (Plan, Do, Check, Act) when he mentioned that work activities and implementation options should be identified in all steps of process safety.

According to the Likert-scale questions, safety programs and guidelines, applied at the facility level, are implemented and reviewed at differing frequencies and with differing priorities, depending on the posed hazards and risks. The direction and application of these guidelines and procedures often originate from realized risks.

One recommendation also given from these responses is that process safety should be differentiated from industrial hygiene. One participant stated:

> "Process safety focuses on loss of containment incidents involving highly hazardous chemicals and other forms of stored energy which can lead to fires, explosions and toxic vapor cloud releases. Major process safety incidents are normally relatively rare events, episodic in nature, with the potential for major onsite as well as offsite consequences. Industrial hygiene focuses on occupational exposures onsite, normally of a repeated,

> ongoing nature which can negatively impact worker health, typically one individual at a time, through occupational illness, impaired health, and wellbeing. Measures taken to prevent loss of containment and process safety incidents may also serve to reduce or eliminate occupational exposures to workplace hazards and vice versa…"

Another participant explained:

> "…Safety leadership and culture drive the systems used to manage both the engineering and administrative controls to keep everyone safe from toxic exposures. Thus, my addition of the term 'Operational Discipline.'"

Major Challenges in Health and Safety Plan Implementation and Improvement

Reducing 'parallel or duplicate programs,' and assessing ever-increasing challenges of achieving zero-incident targets were some major challenges mentioned by the research participants. The concept of zero-incident targets in safety compliance is very widespread phenomenon. While the idea has been around for decades, it was recently adopted in the United States chemical industry by Ashland Company (Ashland, 2018). There has been some critique of the application of this concept among safety professional circles, who argue that while it is an indicator of excellence in safety, it is a lagging indicator of safety that may harbor the suppression of accurate incident reporting through intimidation or bonus and incentive programs.

Additionally, it was mentioned that the stewardship of safety programs is another taxing activity, and is a result of "boundaries of safety programs that extend into inbound raw material and third party contract operations." In other words, while chemical suppliers, vendors, and contractors work on company property to provide goods and services, the host is subject to multi-employer safety compliance obligations. The stewardship of safety programs for a whole range of personnel can be taxing.

Preventive Measures for Worker Exposure Reduction

Among research participants, capital investments in repairs and maintenance of process equipment provided significant reduction in chemical exposures. I have a personal example of this. Recommendations I have made as an Industrial Hygiene consultant enabled necessary repairs and maintenance that reduced source leak potential exposures of 1,3-butadiene from a tanker truck from 1000 ppm to 10 ppm.

Application of Process Hazard Analysis

According to the participants, developing an awareness of process safety principles was invaluable. One participant alluded to the DuPont® model that helps explain the step review process of Process Hazard Analysis:

DuPont® Model of Process Hazard Analysis

Step 1 – Establishing the Safety Culture

Step 2 – Providing Management Leadership and Commitment

Step 3 – Implementing a Comprehensive PSM Program

Step 4 – Achieving Excellence through Operational Discipline

The DuPont Model incorporates the necessity of Auditing, Process Safety Information, Process Hazards Analysis, Operating Procedures and Safety Practices, Management of Technology Change, Quality Assurance, Prestart-Up Safety Reviews, Mechanical Integrity, Management of "Subtle Changes," Training and Performance, Contractors, Incident Investigation, Management of Personal Change, and Emergency Planning and Response (DuPont, 2010).

Strengths and Limitations of Study

Overall, the strengths in this study is that helps to establish various approaches and priorities of professionals in mitigating risks of chemical exposures, which ultimately reinforce the performance of chemical safety programs. A significant strength and feature of this study was the gathering of interviews and the administration of a questionnaire that explore ways that safety professionals communicate regarding safety topics, what types of information is voluntary participation, and to explore the levels of inclusion and stakeholder representation involved in EHS decision-making. Additionally, the results are highly significant as they were generated from original research and are instrumental for further research.

A limitation of this study is its low response rate and very small sample size. Given the low response rate, a decision was made to conduct a qualitative assessment of results, instead of a quantitative assessment as previously planned. The nature of qualitative assessments and their strengths and limitations should be recognized. While qualitative analyses typically ascertain qualities or characteristics, they may effectively enable elemental interpretations useful in developing theory. They also may provide justifications for further quantitative research. (Madrigal, 2012).

Discussion of Findings from Literature Review

Toxicology and Occupational Health

Biological monitoring of polymer workers (e.g., spirometry, medical examinations, and biomarkers from blood testing) can help monitor worker exposure to monomers and is rapidly growing in its ability to detect human physiological aberrations. While this element of occupational health including biological monitoring and spirometry is often contracted out to medical facilities, as evidenced by my research participants, it is important that safety professionals stay informed of this growing science. Pre-employment and periodic medical evaluations, per OSHA regulations, has an important role in this process. It is vital that workers are biologically monitored effectively as the prevalence of breast cancer is still quite alarming for this industry.

The International Agency for Research on Cancer (IARC), and National Toxicology Program (NTP), and the US EPA play an important role in assessing the health risks posed by chemicals as well as identifying the credibility and weight of evidence. The conclusions provided from their bioassays, which determine dose-response relationships from chemical exposures, are continually evolving. Even their classifications of carcinogens are continually changing – formaldehyde, as a specific example, was only recently classified as a carcinogen. These toxicological assessments of chemical risks served as the basis for OSHA regulations of carcinogens and continue to improve appropriate settings for the permissible exposure limits. According to the literature, periods of major shifts in worker safety and health arose through political pressures that balanced risk and provided a regulatory environment that enable protections to innovations in process safety and exposure control (Infante, 2009).

No participant in this study emphasized scientific exposure control principles. According to the literature, while scientific endeavors (toxicology, epidemiology, case studies) are instrumental in determining appropriate levels of risk to chemical exposures, technological feasibility and economic analysis play a more defining role in shaping governmental initiatives and directives (Infante, 2009). Commercially-supported private industries have enabled essential technological and operational innovations that have provided new worker protections and standards, and have even improved workflow and operations efficiencies.

Hierarchy of Controls

The importance of the concept of the hierarchy of controls in industrial hygiene should always be stressed. Process isolation and substitution, and state-of-the-art engineering controls have proven to be remarkable strategies in reduce exposures to monomers. Forced hoods for soldering benches, moveable hoods, and ducts, and enclosures using closed vats are just some example of crucial ventilation technologies that are important to this industry. Laboratory fume hoods were commonly used at these facilities, but surprisingly the study participants did not emphasize engineering controls in their responses.

There are many different types of open-systems in the production and processing of plastics and rubbers that may expose workers to monomers, including injection molding, extrusion, blow molding, calendaring, and compression molding. It is essential that there is effective monitoring and oversight regarding overheating events, machine malfunctions, purging, and maintenance operations. All the research participants worked at scaled-up facilities where closed-loop systems were most prominent, so they did not discuss open-loop systems that are more typically in plastics and rubber processing and recycling facilities.

Process modification and automation have played an enormous role in exposure reduction. A great example is the introduction of automated, close, self-cleaning process vessels in the 1970s that effectively discontinued the practice of manual vessel cleaning, which was an activity where workers would go inside reactor vessels to scrap off polymer residue. Working in vessels was highly dangerous to polymer workers as they could be exposed to monomer concentrations of up to 1000 ppm. As explained in the literature review, this activity was specifically linked to angiosarcoma, a rare liver cancer that existed among vinyl chloride workers. Following the adoption of the 1974 OSHA directive on carcinogens, this regulatory framework enabled and spurred solutions and commercial support for automation technologies that incorporated high-pressure clean-water materials as well as innovative reactor designs. These technologies provided a strategy to meet the 1 ppm OSHA PEL for vinyl chloride.

While “cold” polymerization processes were developed to reduce fugitive emissions (e.g., for butadiene production), they ultimately increased the frequency of manual reactor cleaning. It is thus important for safety professionals to acknowledge direct and indirect consequences of changes in exposure control strategies.

Not only did the 1974 OSHA directive transition protect worker health, it resulted in massive cost savings from product recovery. During this research phase in the 1970s, many other aspects of engineering design came into play, including a variety of reactor cleaning methods, the introduction of larger reactors that reduce cleaning frequency, an improvement in chemical stripping operations, and the installation of more control equipment including interlock systems, gauging, warning lights and alarms. Providing a double-wall pipeline and leak monitors proved to be essential for the control of vinyl chloride materials in particular.

According to the literature, innovations in approaches regarding safety and health do not always require governmental action (Infante, 2009). Governmental action can help reinforce, or provide financial and technological support to the voluntary actions of industry. For example, the transition from high-loss reciprocating pumps to centrifugal pumps and then to double mechanical seals and seal-less pumps occurred without governmental directives. These technologies prompted a remarkable reduction in monomer exposures.

Obviously, the role of PPE, worker protections, education, training, and surveillance should not be overlooked. These defensive strategies are the last line of defense for polymer works and provide necessary employee protection. The continual evaluation of PPE, including chemically-compatible respirators, gloves, and eyewear should be emphasized. Additionally, the development and advancement of training for employees, contractors, and vendors play an ongoing role in exposure control.

Process Safety

There have been many run-away reaction incidents related to the production of vinyl chloride, butadiene, etc. Understanding their root causes can be an important step in monitoring chemical processes and finding gaps in their evaluations. There may be a wide range of root causes, including operator and management errors and inadequate:

1) Operating procedures
2) Knowledge of process chemistry and thermochemistry
3) Engineering design for heat transfer
4) Control systems
5) Safety backups for emergency venting

Other important considerations include studying the production process thoroughly during scale-up and startup operations, understanding the potential for mischarging reactants including overcharging, wrong material, too rapid of addition, wrong sequence of chemical addition, undercharging, temperature control failure, impurities (e.g., water) in raw materials, maintenance-related issues, or operator failure of written procedures.

IX. CONCLUSION

Summary of Thesis Results

This research, in addition to a systemic review of the toxicology of various monomers, established: a representation of the polymer industry, the best practices and preventative measures for chemical exposure reduction in the polymer industries, major exposure control implementation challenges, and the application of product stewardship guidelines (PSGs).

Among the key findings by the research participants were that:

1) Professional discipline is recognized as a key motivator in EH&S, especially during routine evaluation and implementation of safety programs.
2) Cooperation and representation of industry representatives is relatively private.
3) The advancement of worker and contactor training and the retention of experienced workers are highly valued.
4) The commercial availability and support of advanced engineering controls is essential to driving technological advances in exposure control.
5) EH&S activities may be delayed by:
    a. Redundancies in safety programs.
    b. Challenges in achieving zero-incident targets.
    c. Effort to integration third party-stewardship of safety programs.
6) The review and implementation of safety programs that incorporate PSGs
    a. Should be conducted routinely, perhaps monthly.
    b. By various divisions in labor, including supervisors, operators, technicians, and managers.

General Implications of Thesis Results

This research has some profound implications, including its demonstration of a need for a new approach to exposure science and process safety. Results of this study seem to suggest that process safety serves a primary role in securing protection of workers and works in conjunction with industrial hygiene assessments. The synergy of process engineers, industrial hygienists, auditors, and inspectors is important in all steps of risk management and safety program implementation. This suggests that these divisions in labor are important to the efficiency and consistency of assessment and implementation of safety programs, and to the adoption of consensus health and safety standards.

The safety professional needs to reach out to experts in their fields, and to collaborate with many different stakeholders, to be most efficient with the types of activities and programs in which they can consistently and actively engage. Additionally, given the private nature of industry and increasing responsibilities of safety professionals, it is important that consensus standards are consistently reevaluated and repurposed by professional and trade associations, as well as regulatory bodies, in order to most effectively achieve compliance and risk prioritization.

Future Direction of Study

As the future direction of this study, there is much to do to elucidate the workings of the chemical industry – where it has been, where it is now, and where it is going. The history of the chemical industry is important for professionals to understand. EHS professionals should be adaptable and stay up-to-date of the developing sciences surrounding exposure control and process safety. The chemical industry has made remarkable advances in exposure control in the last century, much of which that has been unfortunately forgotten. Efforts were made in this paper to resurrect research from the 1950s through the 1970s that played a crucial role in understanding exposure science.

Given that this research has begun some initial discussion on the need to integrate many aspects of environmental health and safety of monomers, it is important that further research be conducted to test some of the principles and themes of the connection of exposure control and process safety found in this paper. Another topic of research that is on the frontier is the toxicology of monomers and the biomarkers at play. Researchers should further investigate the similarities of monomer species and various effects on the human body, specifically on their CYP450 metabolism into epoxides and quinones. If researchers understood more about this science, we could assert that hundreds of different chemical variations that we are current regulating separately can actually be grouped together as a class for regulatory and scientific purposes, and assist the goals of the Toxic Substances Control Act.

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XII. APPENDICES

Appendix A: Questionnaire

Appendix B: Email Script

Appendix C: Questionnaire Guidance Script

Appendix D: Questionnaire-style Entry #1 – July 23, 2018

Appendix E: Questionnaire-style Entry #2 – June 19, 2018

Appendix F: Interview-based Entry #1 – February 2, 2018

Appendix G: Commentary-style Entry #1 – August 18, 2018

Appendix H: Commentary-style Entry #2 – July 23, 2018

APPENDIX A: Questionnaire Proposal

1. Which of the following chemicals are used in your facility?
   - ☐ Formaldehyde
   - ☐ Ethylene oxide
   - ☐ Butadiene
   - ☐ Vinyl Chloride
   - ☐ Styrene
   - ☐ Benzene
2. What are the areas, job tasks and processes that could contribute to potential chemical exposure to workers [to selected chemical]?
3. What preventative and control measures are currently in place to reduce worker exposure [to selected chemical]? {ventilation, exposure monitoring, PPE, administrative controls, and alarm systems}
4. Could you explain the site strategy to apply training, PPE, and standard operating procedures in achieving exposure reduction?
5. What are the most successful programs and activities that your site has utilized to make progress in exposure reduction?
6. What are some of the major challenges that your site has experienced that have limited progress in developing and implementing EHS directives and programs?
7. Has your site experienced any challenges in receiving financial assistance or technical expertise that would help address exposure control or process safety?
   - ☐ Strongly Agree
   - ☐ Agree
   - ☐ Disagree
   - ☐ Strongly Disagree
   - ☐ Not applicable
8. If you answered *agree* or *strongly agree* to Question 7, what kind of challenges has your company experienced and what needs to be addressed?
9. If you answered *disagree* or *strongly disagree* to Question 7, can you provide how you were able to avoid these kinds of issues?
10. Has there been a recommendation related to control strategies that has not been implemented at the facility because of financial reasons?
11. How have Product Stewardship Guidelines been applied or reviewed during the implementation of facility construction and maintenance or as part of EHS directives related to exposure control and process safety?
12. Is a Process Hazard Analysis Team or Safety Committee at your site?
    - ☐ Yes
    - ☐ No
13. How often does the PHA Team, Risk Management Team, or Safety Committees that addresses monomer exposures meet?
    - ☐ Weekly
    - ☐ Monthly
    - ☐ Bimonthly
    - ☐ Annually
    - ☐ Seldom
14. Could you explain the cooperation between the site's safety committee members with industry specialists and managers as it relates to exposure control and process safety?
15. Do you have examples of shared resources between industry specialists and the safety committee and/or safety managers?
16. How do EHS directives take into account planning for process changes, emergency response, and other non-routine activities?
17. Could you explain any changes over time in the process and routine?
18. How often does the company invest in new PPE to protect workers from monomer exposures during *non-routine* processes?
    - ☐ < 6 months
    - ☐ 6 months-1 year
    - ☐ 1-2 years

☐ 2-3 years
☐ > 3 years

19. How often does the company invest in new engineering or administrative controls to protect workers from monomer exposures during *non-routine* processes?
☐ < 6 months
☐ 6 months-1 year
☐ 1-2 years
☐ 2-3 years
☐ > 3 years
20. How often does the company invest in new PPE to protect workers from monomer exposures during *routine* processes?
☐ < 6 months
☐ 6 months-1 year
☐ 1-2 years
☐ 2-3 years
☐ > 3 years
21. How often does the company invest in new engineering or administrative controls to protect workers from monomer exposures during *routine* processes?
☐ < 6 months
☐ 6 months-1 year
☐ 1-2 years
☐ 2-3 years
☐ > 3 years
22. How often are Local and General Exhaust Ventilations inspected to ensure they are working properly?
☐ Weekly
☐ Monthly
☐ Bimonthly
☐ Annually
☐ Seldom
23. How often does the company request Industrial Hygiene surveys to assess worker exposures?
☐ < 6 months
☐ 6 months-1 year
☐ 1-2 years
☐ 2-3 years
☐ > 3 years
24. Could you describe any recent IH surveys that have made a significant impact on your company as it relates to designing appropriate measures for exposure control and process safety?
25. How frequently are engineering and chemistry evaluations and designs conducted?
☐ Weekly
☐ Monthly
☐ Bimonthly
☐ Annually
☐ Seldom
26. Do you have Occupational Health resources at your facility?
☐ Yes
☐ No
27. If you answer yes, could you characterize the role of those Occupational Health resources in identifying and tracking exposures (e.g., biological monitoring)?

APPENDIX B: Email Script

Hi, my name is Kevin Kearney. I am an Industrial Hygiene and EHS professional in Charlotte, North Carolina. I am seeking participants for my thesis research on “Best Practices of Process Safety in the Plastics Industry.” My research will ensure completion of my Master of Science degree in Environmental Health at East Carolina University.

I was inspired to do this research on polymers while working in the chemical industry. While working as a lab technician for BASF and Henkel Corporation, I had direct experience with polymerization units and production areas for plastic and adhesive polymer resins, including acrylics, styrenic, and butadiene (BD) products. I found it fascinating that there were so many safeguards in place to keep polymer workers safe, such as state-of-the-art alarm and monitoring systems, restricted access procedures, and reactor stripping and automatic cleaning processes. While conducting my thesis literature review, I was intrigued by the development of polymerization reactor technologies. Technologies and strategies to protect workers from exposure to monomers are showing great promise.

Prior to 1974, it was common for workers to manually clean polymer reactor vessels, but following OSHA directives on vinyl chloride, many companies began to develop automatic cleaning systems. Not only did these technologies decrease manufacturing costs, decrease fugitive emissions, and improve production quality, automated reactor systems isolated workers from a particularly dangerous environment, where monomer exposures could be as high as 1,000 ppm. I aim to assess recommendations from industry managers and specialists for how to control and most effectively evaluate monomer exposures in the workplace.

If you would be willing to provide your expertise to my research, I have attached a link below that will direct you to a questionnaire that asks a series of open-ended and multiple-choice questions. You are not required to answer all the questions, and your identification will remain confidential. I have provided documentation of my Thesis Proposal that has been reviewed by the ECU Institutional Review Board (IRB).

If you are interested, please submit answers to my questionnaire by the end of July 2018 via the Questionnaire link or a Microsoft Word document. If you know someone else who may be interested in participating in this study, please forward this email on. Thank you in advance for your participation. If you have any questions, you can call me at 980-621-2437. If you have questions regarding your rights as a research participant, you can call my university Office of Research Integrity & Compliance at 252-744-2914.

Best Regards,

Kevin Kearney

Link to Questionnaire on Best Practices in Process Safety for Monomers
https://ecu.az1.qualtrics.com/jfe/form/SV_bvnQsPedWJTqSAl

APPENDIX C: Questionnaire Guidance Script

To Whom It May Concern,

I would like to provide my initial responses from my survey participants. These may help if providing comments and answers in the survey (I have attached a link on the next page). I'm just looking for some general themes and I would like your input from your years of experience in process safety.

The best practices in Process Safety and Exposure Control elucidated so far lie in the effective use of corporate guidelines and procedures for Standard Operating Procedures (SOPs), Managements of Change (MOCs), Risk Management Plans (RMPs), Safe Work Permitting, and Emergency Response. These guidelines at the facility are applied at varying degrees depending on the posed hazards and risks. The direction and application of these guidelines and procedures often originate from these realized risks.

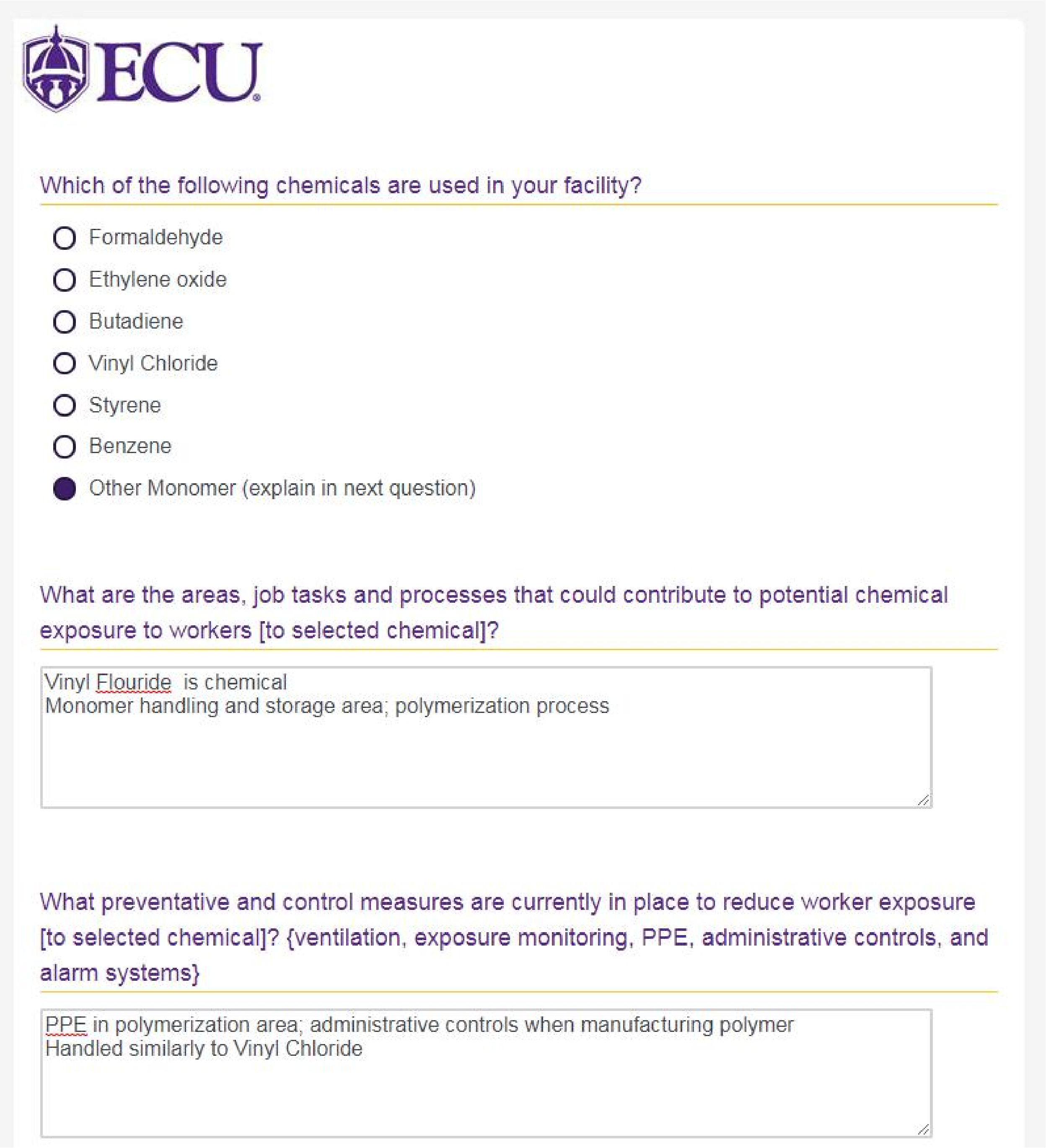
Most progress in exposure reduction has been employee training, which includes audits, self-policing training (e.g., Safe Start), and contractor/vendor training. The developments of the before-mentioned guidelines and procedures have also made a huge difference

Aspects that can be improved industry-wide include reducing "parallel or duplicate programs," assessing ever-increasing challenges of achieving zero-incident targets and enabling and granting the stewarding of programs to third parties. The most demonstrable application of exposure reduction is investments towards installing advanced engineering controls, but the potential of that pursuit lies within commercial availability and support

The biggest challenge to process safety and exposure control is retaining and adapting to the loss of highly experienced personnel. On average it realistically takes about 2 years to adequately train up polymer workers, and the loss of personnel with 35-40 year of experience are often difficult to replace.

Another big element related to this is that the safety culture and leadership drives the systems used to manage both the engineering and administrative controls to keep everyone safe from toxic exposures (operational discipline), and the application of the hierarchy of controls is a very well recognized and pursued concept within process safety.

APPENDIX D: Participant 1, Questionnaire-style Entry #1 – July 23, 2018



Which of the following chemicals are used in your facility?

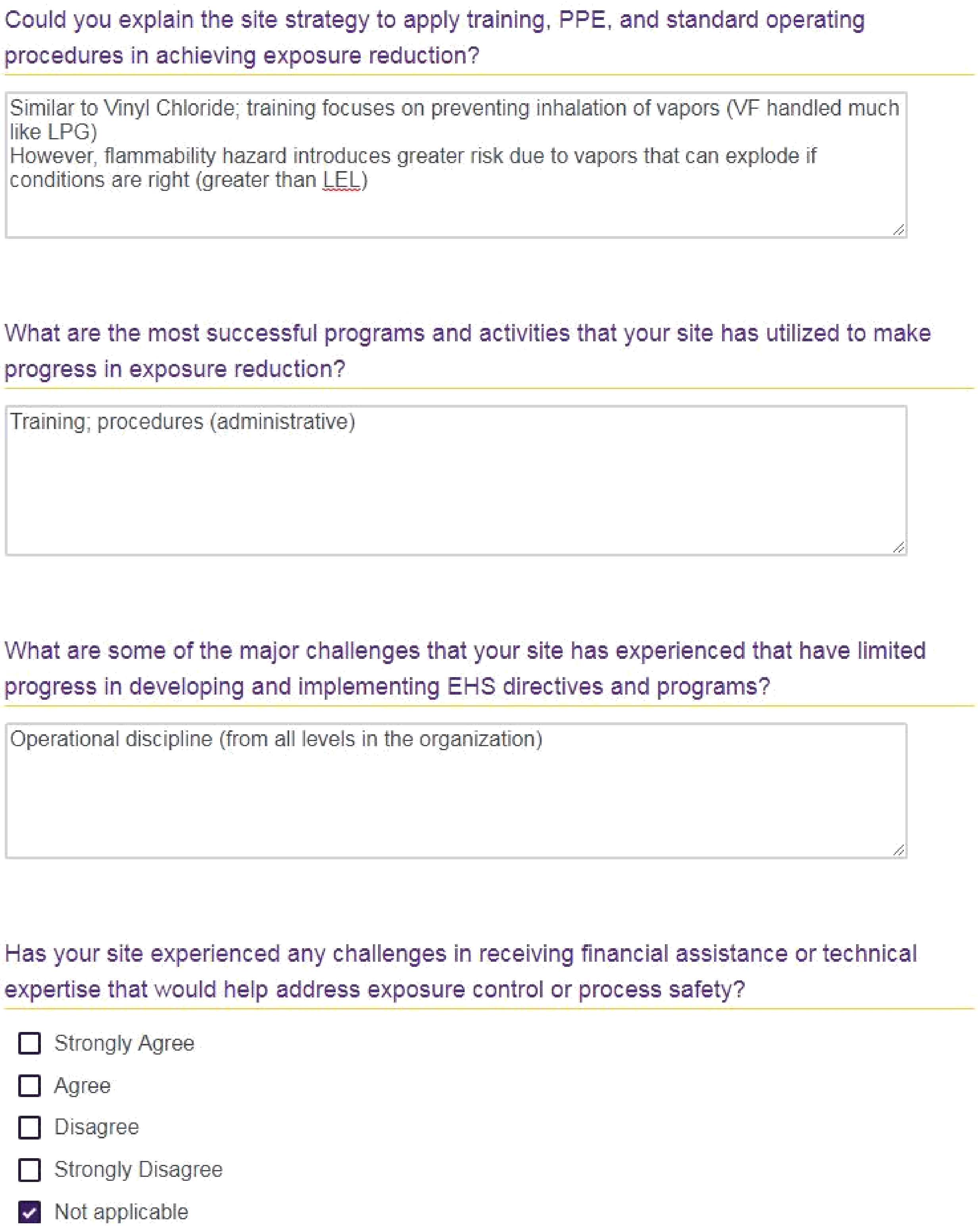
○ Formaldehyde
○ Ethylene oxide
○ Butadiene
○ Vinyl Chloride
○ Styrene
○ Benzene
● Other Monomer (explain in next question)

What are the areas, job tasks and processes that could contribute to potential chemical exposure to workers [to selected chemical]?

Vinyl Flouride is chemical
Monomer handling and storage area; polymerization process

What preventative and control measures are currently in place to reduce worker exposure [to selected chemical]? {ventilation, exposure monitoring, PPE, administrative controls, and alarm systems}

PPE in polymerization area; administrative controls when manufacturing polymer
Handled similarly to Vinyl Chloride



Could you explain the site strategy to apply training, PPE, and standard operating procedures in achieving exposure reduction?

Similar to Vinyl Chloride; training focuses on preventing inhalation of vapors (VF handled much like LPG)
However, flammability hazard introduces greater risk due to vapors that can explode if conditions are right (greater than LEL)

What are the most successful programs and activities that your site has utilized to make progress in exposure reduction?

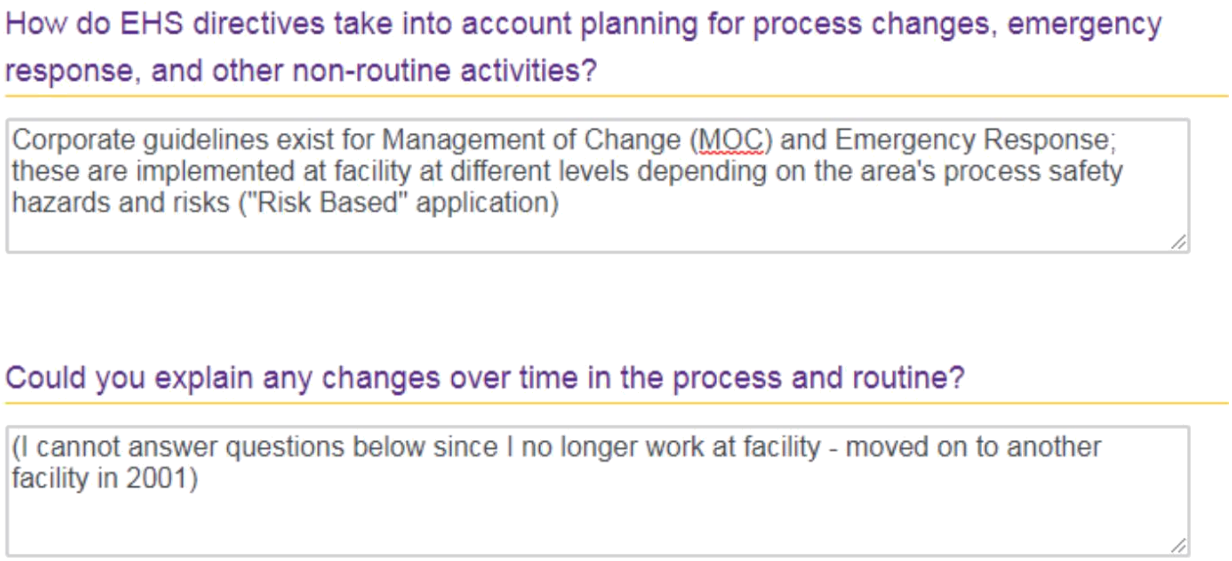
Training; procedures (administrative)

What are some of the major challenges that your site has experienced that have limited progress in developing and implementing EHS directives and programs?

Operational discipline (from all levels in the organization)

Has your site experienced any challenges in receiving financial assistance or technical expertise that would help address exposure control or process safety?

☐ Strongly Agree
☐ Agree
☐ Disagree
☐ Strongly Disagree
☑ Not applicable

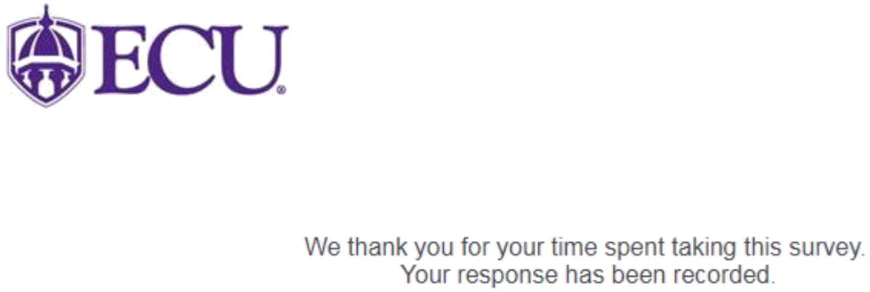


How do EHS directives take into account planning for process changes, emergency response, and other non-routine activities?

Corporate guidelines exist for Management of Change (MOC) and Emergency Response; these are implemented at facility at different levels depending on the area's process safety hazards and risks ("Risk Based" application)

Could you explain any changes over time in the process and routine?

(I cannot answer questions below since I no longer work at facility - moved on to another facility in 2001)



ECU

We thank you for your time spent taking this survey.
Your response has been recorded.

APPENDIX E: Participant 2, Questionnaire-Style Entry #2 – June 19, 2018

1. Which of the following chemicals are used in your facility? Styrene & Butadiene

2. What are the areas, job tasks and processes that could contribute to potential chemical exposure to workers [to selected chemical]?

   Solution preparation, lab scale reactor charging, recovery of polymer at end of polymerization.

3. What preventative and control measures are currently in place to reduce worker exposure [to selected chemical]? ventilation, exposure monitoring, PPE, administrative controls, and alarm systems.

   All of the above apply plus reactor automation. Admin controls are executed through standard operating procedures, management of change, and safe work permitting. Specifics are likely confidential.

4. Could you explain the site strategy to apply training, PPE, and standard operating procedures in achieving exposure reduction?

   That's a broad question - difficult to be concise. We follow an industry typical progression of hazard elimination if possible followed by risk mitigation through engineering controls, admin controls, with PPE being purely defensive - PPE not intended to be directly chemically exposed during normal operations. Operating procedures are regularly reviewed and revised by team to ensure accuracy and reinforce operator knowledge.

5. What are the most successful programs and activities that your site has utilized to make progress in exposure reduction?

   Highest impactor is training for sure. Employee training from both an interdependent and independent point of view. e.g. Both lab & procedural audits in addition to self-policing by initiatives like Safe Start. Chemical hazard and modes of exposure. Contractor training. Vendor training.

6. What are some of the major challenges that your site has experienced that have limited progress in developing and implementing EHS directives and programs?

   a. Number of parallel programs is a consideration. New programs are appreciated from taking a different slant on running topics, but old non-critical programs should be moved off the list to avoid the message being lost by dilution.
   b. Approaching true zero incident targets takes increasing effort.
   c. Stewarding programs to third parties in chemical industry becomes essential as boundaries of programs extend to inbound raw materials and third party contract operations.

7. Has your site experienced any challenges in receiving financial assistance or technical expertise that would help address exposure control or process safety?

   Agree

8. If you answered agree or strongly agree to Question 7, what kind of challenges has your company experienced and what needs to be addressed?

    Highest level of safety for me is achieved by advanced safety instrumented functions, which are expensive and must develop in parallel with commercial support.

9. If you answered disagree or strongly disagree to Question 7, can you provide how you were able to avoid these kinds of issues?

    N/A

10. Has there been a recommendation related to control strategies that has not been implemented at the facility because of financial reasons?

    Yes, related to answer in #8.

11. How have Product Stewardship Guidelines been applied or reviewed during the implementation of facility construction and maintenance or as part of EHS directives related to exposure control and process safety?

    Yes – we cover this under our step review program.

12. Is a Process Hazard Analysis Team or Safety Committee at your site?

    Safety committee only as this is a lab site. PHA team would be typical for a production site.

13. How often does the PHA Team, Risk Management Team, or Safety Committees that addresses monomer exposures meet?

    Monthly

14. Could you explain the cooperation between the site's safety committee members with industry specialists and managers as it relates to exposure control and process safety?
    Forum convened annual. Topical specific interactions regular as needed.

15. Do you have examples of shared resources between industry specialists and the safety committee and/or safety managers?

    Not sure exactly what's being asked. One possibly relevant example – We informed PPE manufacturer about combined chemical solubility hazards towards penetration time so they could develop better gloves for us. E.g. Chemical A and chemical B both specify glove type X. However a blend of A+B may behave very different and penetrate quickly.

16. How do EHS directives take into account planning for process changes, emergency response, and other non-routine activities?

    Again, a very broad question – changes primarily MOC or capital request is the first bucket to identify larger impact items. Emergency response is dealt with by local HazMat fire department team. We have regular meetings to discuss hazards on site.

17. Could you explain any changes over time in the process and routine?

This is a research site that stewards manufacturing technology to production sites around the world. Change is the daily task. Highest level our exposure safety now targets realistically target and most often achieve a true zero. This was unrealistic 5 years ago.

18. How often does the company invest in new PPE to protect workers from monomer exposures during non-routine processes?

    a. < 6 months

19. How often does the company invest in new engineering or administrative controls to protect workers from monomer exposures during non-routine processes?

    a. 6 months-1 year (answered with respect to site, not company)

20. How often does the company invest in new PPE to protect workers from monomer exposures during routine processes?

    a. < 6 months

21. How often does the company invest in new engineering or administrative controls to protect workers from monomer exposures during routine processes?

    a. 6 months-1 year (answered with respect to site, not company)

22. How often are Local and General Exhaust Ventilations inspected to ensure they are working properly?

    a. Monthly. PM program indicates quarterly failure rate.

23. How often does the company request Industrial Hygiene surveys to assess worker exposures?

    a. < 6 months – rolling audits by chemistry & process.

24. Could you describe any recent IH surveys that have made a significant impact on your company as it relates to designing appropriate measures for exposure control and process safety?

    a. No. Only one hit in last decade. Cause of hit was understood and did not warrant a change to the program.

25. How frequently are engineering and chemistry evaluations and designs conducted?

    a. On demand – roughly weekly for chemistry and 6 months to 5 years on engineering.

26. Do you have Occupational Health resources at your facility?

    a. No – outsourced to third party.

27. If you answer yes, could you characterize the role of those Occupational Health resources in identifying and tracking exposures [e.g. biological monitoring]?

APPENDIX F: Participant 3, Interview-Based Entry #1 – February 2, 2018

1. Which of the following chemicals are used in your facility?
    a. Styrene, 1,3-Butadiene, Methyl Methacrylate (MMA), Butyl Acrylate (BA), and 2-Ethylhexyl Acrylate (2EHA).

2. What are the areas, job tasks and processes that could contribute to potential chemical exposure to workers [to selected chemical]?
    a. Trucks, Butadiene Tanks, Reactors
    b. Styrene and 1,3 Butadiene are brought in by tanker car
    c. Solution preparation, lab scale reactor charging, recovery of polymer at end of polymerization.
    d. Rupture and catch tanks, Reactor Area
    e. Styrene and Butadiene to SP Acrylic resin (Stripper)
    f. Storage Tanks to Condenser and Decanter to Boiler (natural Gas) and Flare (Back-up)
    g. Thermal Oxidization
    h. Waste water stripping
    i. Single and double state vacuum to condenser
    j. Temporarily Toting off latex – non PSM

3. What preventative and control measures are currently in place to reduce worker exposure [to selected chemical]? ventilation, exposure monitoring, PPE, administrative controls, and alarm systems.
    a. Leak detection for BD
    b. PLC – interlock, no alarms, quarterly maintenance, camera and video from control room, operator overrides go to supervisor for approval

4. Could you explain the site strategy to apply training, PPE, and standard operating procedures in achieving exposure reduction?
    a. Onboarding Safety Training – 2-week training – Supervisor reads and signs off.
    b. Airgas company does safe handling training for Ammonia
    c. Forkift training
    d. Training compliance matrix
    e. Hot work permitting (supervisor and maintenance manager)
    f. Control Room (Permitting for Line Break and Confined Space) – 1 man
    g. Behavior-based Safety Committee Observation Form

5. What are the most successful programs and activities that your site has utilized to make progress in exposure reduction?
    a. Establishing the source of a leak at a tanker truck – effectively changed the requirements of maintenance.

6. What are some of the major challenges that your site has experienced that have limited progress in developing and implementing EHS directives and programs?
    a. 2 years to really get operator trained up - (35-40 years of training hard to replace)

7. Has your site experienced any challenges in receiving financial assistance or technical expertise that would help address exposure control or process safety?
    a. N/A

8. If you answered agree or strongly agree to Question 7, what kind of challenges has your company experienced and what needs to be addressed?
    a. N/A

9. If you answered disagree or strongly disagree to Question 7, can you provide how you were able to avoid these kinds of issues?
    a. N/A

10. Has there been a recommendation related to control strategies that has not been implemented at the facility because of financial reasons?
    a. N/A

11. How have Product Stewardship Guidelines been applied or reviewed during the implementation of facility construction and maintenance or as part of EHS directives related to exposure control and process safety?
    a. Every 5 years, the PHA team meets in incorporates these guidelines in the step review process

12. Is a Process Hazard Analysis Team or Safety Committee at your site?
    a. Process Safety Team – Maintenance Manager, Plant Manager, 2 Chemical Operators, and 2 Supervisor, and the Quality Lab

13. How often does the PHA Team, Risk Management Team, or Safety Committees that addresses monomer exposures meet?
    a. RMP – Risk Management Plan (What If's) – every 5 years
    b. Risk Score – Frequency Likelihood and Consequences
    c. Quarterly – Hazardous waste, PSM, and confined space

14. Could you explain the cooperation between the site's safety committee members with industry specialists and managers as it relates to exposure control and process safety?
    a. I was actually interviewing this safety manager as I was providing industrial hygiene assessments for simultaneously. This client has a strong relationship between industry specialists.

15. Do you have examples of shared resources between industry specialists and the safety committee and/or safety managers?
    a. N/A

16. How do EHS directives take into account planning for process changes, emergency response, and other non-routine activities?
    a. Pre-Startup Safety Review (PSSR)
    b. Management of Change (MOC)
    c. PSM Permit

17. Could you explain any changes over time in the process and routine?
    a. New

18. How often does the company invest in new PPE to protect workers from monomer exposures during non-routine processes?
    a. <6 months

19. How often does the company invest in new engineering or administrative controls to protect workers from monomer exposures during non-routine processes?
    a. As needed

20. How often does the company invest in new PPE to protect workers from monomer exposures during routine processes?
    a. Periodically- Cintas comes to provides – Half face MSA respirators – Full face for line breaks, SABA confined space

21. How often does the company invest in new engineering or administrative controls to protect workers from monomer exposures during routine processes?
    a. Not regularly, as needed.

22. How often are Local and General Exhaust Ventilations inspected to ensure they are working properly?
    a. Maintenance – calibrator of BD styrene; Styrene per quarter – visual exchangers – reactors
    b. PLC – interlock, no alarms, quarterly maintenance ,
    c. Maintenance – Double block and bleed (DBB)

23. How often does the company request Industrial Hygiene surveys to assess worker exposures?
    a. As needed, with new process changes; 3-5 years – consultant to use PPE

24. Could you describe any recent IH surveys that have made a significant impact on your company as it relates to designing appropriate measures for exposure control and process safety?
    a. Better scrubbing, WWTP – waste water treatment plant, Throx, Flare.

25. How frequently are engineering and chemistry evaluations and designs conducted? 3-5 years

26. Do you have Occupational Health resources at your facility?
    a. No.

27. If you answer yes, could you characterize the role of those Occupational Health resources in identifying and tracking exposures [e.g. biological monitoring]?
    a. N/A

APPENDIX G: Participant 4, Commentary-Style Entry #1 – August 18, 2018

…I do not feel it appropriate that I participate in your survey as I am not currently working in or associated with a facility which manufactures or processes polymeric materials. I have reviewed your summary of survey results from participants and offer these comments:

•My understanding is that the title of your thesis is: “Best Process Safety Practices in the Plastics Industry” and your objective is: “… to assess recommendations from industry managers and specialists for how to control and most effectively evaluate monomer exposures in the workplace.” I assume, though not stated in the information provided, that your approach in meeting this objective is to first compile recommendations received from your survey respondents and then assess the effectiveness of these recommendations. I encourage you to use recognized survey techniques and statistical methods in compiling and analyzing the results.

•Regarding your assessment of the effectiveness of recommendations obtained from your survey, it is not evident what techniques and data you will use to carry out your assessment. It will be important to those reading your thesis to know the nature and validity of your assessment process. You may find it useful to categorize and assess your recommended practices according to CCPS’s 20 elements of risk based process safety. These elements are described in the CCPS publication: “Guidelines for Risk Based Process Safety”. A summary as well as the full text can be obtained by referring to the CCPS website @ www.aiche.org/ccps Listed with each element are: 1) key principles and essential features, 2) work activities and implementation options, and 3) performance and efficiency improvement examples. The combination of essentials and improvement examples provide a good understanding and benchmark as to what CCPS recognizes and accepts as good industry practice for each element.

•It might be helpful to define and discuss the two areas you have chosen to study for your thesis – process safety and industrial hygiene. As I’m sure you know, process safety focuses on loss of containment incidents involving highly hazardous chemicals and other forms of stored energy which can lead to fires, explosions and toxic vapor cloud releases. Major process safety incidents are normally relatively rare events, episodic in nature, with the potential for major onsite as well as offsite consequences. Industrial hygiene focuses on occupational exposures onsite, normally of a repeated, ongoing nature which can negatively impact worker health, typically one individual at a time, through occupational illness, impaired health, and wellbeing. Measures taken to prevent loss of containment and process safety incidents may also serve to reduce or eliminate occupational exposures to workplace hazards and vice versa. Developing and describing this synergy will be helpful to the reader of your thesis in understanding why you are focusing on both areas and their respective safe practices in your survey.

APPENDIX H: Participant 5, Commentary-Style Entry #2 – July 23, 2018

Kevin,

…At present, I have not had any luck with locating folks who have time to respond.

Your analysis of the results you did get is consistent with my experience over the years. My only addition is the fact that safety leadership and culture drives the systems used to manage both the engineering and administrative controls to keep everyone safe from toxic exposures. Thus, my addition of the term "Operational Discipline."

As you know, the hierarchy of controls begins with inherently safer designs, engineering controls are next, then administrative controls, and finally, PPE. If you are aware of this hierarchy, great! If not, let me know and I will be more than happy to point you to some references.

And please keep in touch. I will look forward to hearing from you on your progress (and graduation!