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PROCESS EMISSIONS OF PLASTIC OPERATIONS

Protocols for Source Sampling of Organic Gases
Generated during Plastic Processes

FINAL REPORT

TO:

The Society of the Plastics Industry, Inc.

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July 18, 1992

ULRF Project No. 09-5381

TABLE OF CONTENTS

EXECUTIVE SUMMARY

The objective of these experiments was to identify the best collection and analytical techniques available to conduct source sampling during plastics processing, and use them to prepare sampling protocols. Source samples of emissions from polymers in various processes were obtained in order to choose a set of target substances that would be representative of emissions in industrial settings. The study of previously published reports and the detection of emissions from seven plastic processes and five polymers permitted a reasonable basis to choose the target substances.

The target substances recommended to be routinely sampled from five commercial grade plastic materials studied were : for polystyrene (PS): styrene, ethylbenzene, toluene and benzene; for polyethylene (PE): formaldehyde, formic acid and benzene; for acrylonitrile-butadiene-styrene (ABS): styrene, xylene, toluene and acrylonitrile; for polyvinyl chloride (PVC): *vinyl chloride, *hydrochloric acid, benzene and toluene; and for unsaturated polyester bulk molding compound (BMC): styrene. Solid condensation aerosols were also measured in most experiments, therefore total aerosols were also recommended for routine sampling of process emissions. Criteria for selection of target substances were: positive identification, being present above ten times the detection limit of the analytical method and having regulatory interest. (Note: compounds marked with an asterisk were sampled but not detected in these experiments but are nonetheless recommended for routine sampling).

These initial procedures represent the necessary preliminary steps to be the basis for a complete protocol to quantify emissions to be used by the plastics industrial processor. The methods of collection were standard industrial hygiene sampling methods. Analysis was conducted by a commercial analytical laboratory accredited by the American Industrial Hygiene Association (AIHA) and the Commonwealth of Massachusetts.

Samples were taken for seven basic plastic processes and one compounding operation as follows: Extrusion processes: strand ; sheet; blown film and extrusion coating, Injection molding, Thermoforming and Compression Molding, (including a compounding operation).

The focus of the process emissions evaluated in this project is the emissions generated by the melting of the polymer per se. Emissions originated from additives (e.g., stabilizers, chain transfer additives, plasticizers and colorants) may appear in the results but are not the focus of this study. The methods described here are only suitable to evaluate emissions of thermoplastic processes where the polymers are melted in a normal steady state operation or the compounding and cure of the thermoset polyester. Non-steady state operations, such as purging may generate additional decomposition products of industrial hygiene interest. Their generation during plastic production should be evaluated but their collection and analysis were beyond the scope of this study.

I. INTRODUCTION

A. Objectives and Scope

This report presents the results of the first phase of the development of a protocol to characterize emissions generated during plastic processes. The initial task in this project was to identify and perform quantitative analysis on selected organic vapors and measure gravimetrically aerosols generated from some plastic processes. The emissions were collected at the peak off-gassing stage of the plastic production cycle. The sampling strategy consisted of the collection of **source sampling** using industrial hygiene sampling collection equipment on industrial size plastics production machinery at the University of Massachusetts Lowell. The collection and analytical methods described here could be generalized and applied to the identification and relative quantification of organic vapors and aerosols originated from a plastic melt. Once a broad spectrum of organic chemicals was identified and their relative concentrations determined, a decision was made to choose **target substances** suitable for quantification of emissions. These choices were based on two criteria; i.e., the relative amounts produced and the regulatory interest of the substances identified. This initial work is the necessary preliminary steps to be the basis for a complete protocol to quantify emissions to be used by the plastics processor. The methods of collection were standard industrial hygiene sampling methods. Analyses were conducted by a commercial analytical laboratory accredited by the American Industrial Hygiene Association (AIHA) and the Commonwealth of Massachusetts. The objective of this arrangement was to make these procedures available to any plastics processor on a routine basis.

Samples were taken for seven basic plastic processes and one compounding operation as follows: Extrusion processes: strand ; sheet; blown film and extrusion coating, Injection molding, Thermoforming and Compression Molding (including a compounding operation). Five commercially available plastic materials were used for different processes. They were: polystyrene (PS), polyethylene (PE) (high density polyethylene (HDPE) and linear low density polyethylene (LLDPE)), acrylonitrile-butadiene-styrene (ABS), polyvinyl chloride (PVC) and unsaturated polyester BMC (UP).

A total of 30 sample sets were collected to identify organic chemicals through gas chromatography/mass spectrometry (GC/MS) methods. These identified a grand total of 76 quantifiable analytes (relative to a MS calibrating chemical). Two additional sample sets were collected to identify oxygenated compounds from PE extrusion. The analytical technique for these two last sets was High Pressure Liquid Chromatography /Ultra Violet (HPLC/UV). Eight quantifiable aldehydes and organic acids were identified. Aerosols generated from some processes were measured gravimetrically as total aerosols (15 samples) and benzene soluble aerosols (17 samples) for a total of 32 aerosol samples.

The focus of this project was the emissions generated by the melting of the polymer per se. Emissions originated from additives (e.g., stabilizers, chain transfer additives, plasticizers and colorants) may appear in the results but are not the focus of this study. Their generation is not discussed in this report, since their chemical nature and purpose was not identified to the researchers in any of the commercial grade polymers used in the experiments. The methods described here are suitable to evaluate emissions of thermoplastic processes where the polymers are melted in a normal steady state operation

or the compounding and cure of the thermoset polyester. Operations like purging (before and after steady state production) generate additional decomposition products (1). Emissions from thermal decomposition of additives, mold releases and decomposition products generated during purging and non-steady state conditions may be of particular industrial hygienic interest. Their generation during plastic production operations should be evaluated but their collection and analysis were beyond the scope of this report.

B. Review of the Literature

In the production of most plastics, polymers are melted and then shaped in processes such as extrusion, injection molding and thermoforming to obtain the desired final form. During processing, the hot polymer undergoes thermal degradation with the generation of various chemical species. The mechanisms of polymer degradation by heat have been identified as: random chain scission, elimination and de-polymerization (1).

In the presence of air, some hot polymers emit oxygenated degradation products. Laboratory studies of mechanisms of thermal oxidation of some polymers have shown the production of low molecular weight (from one to three carbons) oxygenated forms, such as aldehydes, ketones and organic acids (2).

De-polymerization has as its principal degradation product the monomer or monomers forming the polymer chain. A second mechanism of monomer generation is the release of un-reacted monomer trapped in the plastic material (1).

The variables controlling the generation of emissions have been reported to be: a) the operating temperature; b) the rate of melted mass produced; c) the surface area of the

melted product; and d) the polymer residence time in the processing machine (3), (3). Very few systematic evaluations of thermoplastic process emissions are found in the literature where industrial size machinery has been evaluated. Studies in the U.S. are mostly laboratory evaluations (5) or studies of products of pyrolytic decomposition (6). Three U.S. field studies of thermoplastic emissions from styrene containing polymers were found in the literature (7), (8), (9).

More extensive laboratory and field industrial hygiene evaluations of thermoplastic processes emissions were conducted in Scandinavian countries by the Swedish Work Environment Fund (4), (10), (11). The organic vapors were collected in charcoal tubes and analyzed mostly by GC (no MS) and High Pressure Liquid Chromatography (HPLC). There is no detailed description of the plastic processing machinery (4). No information is provided on what specific process (e.g., injection molding, extrusion, etc.) generated what level of contaminant. The polymers used were commercial plastics of European origin (3).

II. MATERIALS AND METHODS

A. Description of Machinery and Operating Conditions

Sampling collection took place at the University of Massachusetts Lowell, Plastics and Composite Development Center (UML-PCDC) located in the College of Engineering. UML-PCDC has complete processing machinery and testing materials for a vast selection of plastics. The processing equipment used was industrial size. Industrial quantities of technical grade materials and industrial production routines were employed. The UML-PCDC facilities are equivalent to a medium size industrial plastics production facility.

The characteristics of the plastics process machinery used in this project are summarized in Table I. The materials used in each machine are also identified in the same Table. A description of each plastic used appears in Table II.

Operating conditions, such as temperatures, flow rates and sample times are presented in the results section corresponding to each process and raw material (Tables V to XIII). As indicated in Table I, all the UML-PCDC laboratories are equipped with General Exhaust Ventilation (GEV). In addition, three pieces of equipment (the injection molding machine, the thermoforming press and the compounding mixer) have Local Exhaust Ventilation (LEV). The ventilation status of the machinery was not relevant to the sampling conducted in this project. The objective was to bypass any LEV or GEV system by placing sample probes within six inches of the molten polymer.

B. Description of Plastic Raw Material Used

Commercially available plastics were used in the 30 sampling campaigns. Each plastic was used in the specific process for which it was recommended in the supplier's specifications. No quantitative information on additives was provided by the manufacturers. The plastics used by process appear in Table II.

C. Description of Sample Collection and Analytical Methods

A typical experimental run took place on days when no other processes or machines were in operation at the UML-PCDC. Prior to the initial warmup period of a processing machine, a background sample was collected to identify any lingering laboratory air contamination around the processing area. The organic chemicals found in the background sample were subtracted from the final results of the process sample taken during steady state operations. Once the background laboratory air sample was collected, the process machine warmup was initiated. When the recommended operational temperatures, pressures and flow rates were stabilized, steady state was reached and the process sample was collected. It took from one to two hours, depending on the process and the polymer, before steady state was reached. Between 30 and 60 minutes after steady state was achieved, the sampling procedure was started (Precise sampling times and other aspects of sample collection are described in detail when specific methods are described below). This methodology was followed for all sampling campaigns where the analytical method was GC/MS, as well as when the analytes were aldehydes or organic acids. A detailed description of the procedures follows.

1. Sampling for Organic Vapors via GC/MS Analysis

a) Sample Collection

Different thermal desorption tubes were used depending on the analyte. Either a **Carbotrap* 300** tube(for aromatics) or a **Carbotrap 200** tube (for aliphatics), was used as the collection device to capture emissions generated in the processes studied. Figures 1 to 5 in Appendix A illustrate the sample probe locations for an injection molding experiment (Figure 1); for an extrusion paper coating experiment (Figure 2); for an extrusion blown film experiment (Figure 3); for a thermoforming experiment (Figure 4) and for a low pressure compression molding experiment (Figure 5). Details of the Carbotrap tube are shown in Figure 6 (12). The sampling methodology is standard industrial hygiene practice used routinely by the Occupational Safety and Health Administration (OSHA), the Environmental Protection Agency (EPA) and the National Institute for Occupational Safety and Health (NIOSH) and is described in detail in readily available references (13).

(* Note: **Carbotrap** is a trade name of Supelco a subsidiary of the Rohm and Haas Co.).

1) Sample Train The sample train consists of: 1) a Gillian Air Sampling Pump calibrated to draw air at 100 cm^3/min. (calibration procedures appear in Appendix D); 2) **Tygon** tubing connecting the pump to the adsorption tube ; and 3) the Carbotrap tube (**Carbotrap 300 or 200**). The configuration is similar to Figure 7.

Once the sample was taken (usually between 5 and 6 liters of air) the tube was capped and sent to the laboratory for analysis.

2) Sampling Procedure The sample collector (**Carbotrap** tube) is placed approximately 6 inches from where the molten plastic exits the process machine. The sample collectors were placed as close to the hot plastic as practicable, to assure capture of the plume of vapors emitted from the molten material. For details of each collection point see Figures 1 to 5. Three samples were collected for each experiment as follows: first, the sample of laboratory air collected one hour before the initiation of the melting process to assess the extent of contamination of the experimental area; second, the sample of the emission plume at least 30 minutes after the process was equilibrated at steady state for temperature, pressure and flow rates; third, a blank sample (unused sample tube) was shipped to the analytical laboratory with every sample set. The analytical laboratory was not provided with information about which tubes were samples or blanks in order for them to be able to perform blind analysis. Other sampling details by process appear in the description of each experiment.

At the end of each sampling campaign, the emissions, background and blank samples were shipped to the laboratory where they were analyzed within 48 hours of collection as recommended by NIOSH (See NIOSH Method S 1501). Samples were kept under refrigeration (38°F) while awaiting analysis.

b) Analytical Procedure

The Carbotrap tube is desorbed "ballistically" (from 35 °C to 335 °C in 16 seconds) in a Thermal Desorption Unit (Supelco TDU). The effluent is rapidly transferred to the GC column for separation. The GC column was a SUPELCOWAX 10 capillary. This column separates the organic chemicals in the sample (11). The MS procedure follows

immediately after the GC separation. The effluent is passed through a MS detector for identification and quantification of the organics in the sample. The MS quantification of the substances in the sample is made by comparison with a calibrating substance (e.g., benzene). Results are reported as mass equivalent of the calibrating chemical (14).

Carbotrap 300 was used when aromatic organics emission were expected. This was the case for emissions from PS, ABS and polyester BMC. A Carbotrap 200 column was used in situations where aliphatic or polar organics were expected (PE and PVC)(15). After sample collection the sampler was thermo-desorbed and analyzed by GC/MS as explained above. The analysis was performed in accordance with **EPA Method 624** for Volatile Organics. Sensitivity and other data of the analytical method appear with the information supplied from the analytical laboratory in Appendix B. Complete copies of all the analytical methods appear in Appendix D. This analytical methodology was chosen because it permits complete desorption by heat and is sensitive to very low quantities of organic chemicals (13).

2. Sampling for Aldehydes

Vapors from emissions are collected in the locations illustrated in Figures 1, 2 and 3. The collection device consisted of two impingers (bubblers) in series containing a solution of iso-octane and di-nitrophenyl hydrazone. Air was sampled through the bubblers for one hour at a rate of 1 L/min. The solution was then quantitatively evaluated by High Pressure Liquid Chromatography/Ultraviolet (HPLC/UV). The procedure used was **EPA Method TO-5** (Impinger Collection, HPLC/UV). This method was selected because it is specific for aldehydes and unlike GC/MS, the results are not reported as mass equivalents

of a surrogate compound. A complete copy of the method is included in Appendix D.

3. Sampling for Organic Acids

Vapors from emissions were collected in the locations illustrated in Figures 1, 2, 3 and 4 using a silica gel adsorption tube. The sampling train was identical with the one used with Carbotrap tubes (see above). For analysis, the vapors were desorbed with de-ionized water and analyzed using HPLC. The column used was an Aminex HPX-87H ion exclusion column. The solvent was 0.01 H_2SO_4 at 1 ml/min. This method was recommended by the H&ES Analytical Chemistry Laboratory of the Dow Chemical Company, Midland MI (16). This method is a variation of **OSHA Method 28** for organic acids (see copy in Appendix D).

4. Sampling for Aerosols

a) Total Aerosols

The Total Aerosol designation in industrial hygiene practice include solid particles regardless of size, i.e., include respirable and not respirable sizes. They are collected in a filter with no size selective device preceding the sample train. Total aerosols were collected in the locations described in Figures 1, 2 and 3. The sampling train is described in Appendix A, Figure 8. The polystyrene cassette holds 37 mm diameter filters. The cassette was open for sampling to the laboratory air. The filter was a PVC 5 um pore membrane tared filter. Air was sampled for one hour at 2 L/min. After 24 hours of filter drying in a desiccator, the sample was weighed to 0.01 mg. The method used was **NIOSH Method 0500**. A copy of the procedure is included in Appendix D.

b) Benzene Soluble Aerosols

This method was used for the purpose of differentiating organic from inorganic (dust) aerosols. Benzene soluble aerosols represent the organic vapors condensed in the particles collected. It is measured as the weight of the benzene soluble fraction of the Total Aerosols collected. Benzene Soluble Aerosols represent then, the sum of organic aerosols collected in a filter plus the condensed organics from the gaseous emissions that are soluble on benzene. Therefore, the weight of emissions collected by this method could, in some cases, be greater than the solid products of condensation collected by the method of Total Aerosols above. The procedure used for collecting Benzene Soluble Aerosols is identical to Total Aerosols, except that a Teflon (PTFE) 2 um size tared filter was used in a sealed cassette. For analysis, the filter was washed with pure benzene and the benzene soluble materials were determined gravimetrically. The method used was **NIOSH Method 5023.** A complete copy is included in Appendix D.

This sample technique permits analysis for the presence of semi-volatile organic air compounds that could be present in the vapor or particle phases of thermal emissions.

c) Lead Aerosols

The same procedure was used for lead as outlined above for Total aerosols. The analytical method for lead analysis is Atomic Absorption Spectrophotometry (AA). This procedure to detect lead aerosols was used in processes where the raw material was PVC. The method used was **NIOSH Method 7082.** A copy is included in Appendix D.

5. Sampling for Hydrochloric Acid

Samples were collected on silica gel adsorbent tubes following the procedure outlined for organic acids. Sampling was for one hour at 100 cm^3/min. The tubes are desorbed and analyzed by Ion Chromatography. The method used was **NIOSH Method 7903.** A copy is provided in Appendix D.

III. RESULTS

A. Organic Emissions Identified by Process

Seven sampling campaigns measured emissions from four different extrusion processes. They were: a) strand; b) sheet; c) blown film and d) extrusion paper coating. The polymers studied were PS, PE, ABS and PVC. A list of the organic chemicals identified in these processes appears in Table III. Sampling procedures and methodology were described above. Diagrams of sampler locations appear in Appendix A.

Two selection criteria for GC/MS analysis results were fulfilled by the chemicals identified in the table: first, the chemical had to be positively identified by the analytical method, and second, it had to be present in an amount ten times the detection limit. This criteria was considered to be adequate since the background concentrations measured in the laboratory air were less than 1/10 the detection limit of the method (>0.001 ugm) and generally this amount identified the target substances of interest.

Aldehydes and organic acids in the PE experiments were identified by a different collection and analytical method, i.e., HPLC/UV (see Tables VII and VIII). The procedures in these experiments were quantitative and specific for aldehydes and organic acids.

Table IV shows the emissions identified in three processes: a) injection molding; b) thermoforming and c) compression molding. Five polymers were studied: PS, PE, ABS, polyester BMC and PVC.

Identical selection criteria apply for this table as applied to Table III.

B. Organic Emissions by Polymer

Tables V to XI show the relative mass percentage of organic chemical emissions during the steady state processes studied and analyzed by GC/MS and HPLC/UV. The values in the tables were calculated by dividing the amount of each component by the total of all these identified components plus all other measured but un-identified components. Thus comparisons can be made within each experiment to examine the relative amounts of the various emissions. It was not possible to calculate any absolute amounts of emissions, per unit of polymer processed. This was because although the sample collected was representative of the emission stream, it did not contain the total emissions generated, or even a known proportion of the emissions. Therefore, it was not possible to compare the amount of emissions from one process, e.g., extrusion with another such as thermoforming.

The relative emission percentages are calculated as the proportions by weight of the emission amounts of a compound in micrograms per kilogram of melted polymer going through the plastics process machine. Emission amounts were measured during the sampling time at steady state. The same sampling and analytical instruments and techniques (GC/MS) and (HPLC/UV) were used for each series of experiments with each polymer in the various plastic processes studied.

The tables of results also present the highest temperature recorded during the process. The profile of operating temperatures typically varies between 5 and 20 °F below the value reported in the Tables. However, it was considered that the critical parameter for the generation of emissions is the highest recorded temperature in the process.

It also should be observed that the mass of vapors collected during the sampling process is not a stoichiometric amount of the total mass of vapors emitted during a given process. The amounts collected during each sampling period were a fraction of the total emissions generated by the melted polymer during the process. The total emission plume was not collected, and the sample points chosen were but one of the sources of emissions (probably the highest) so that the total amount of emissions should be, by logic, higher that the amounts reported here. It is also important to point out that the percentage emissions are steady state values that ignored purging at the beginning and end of the processes and did not involve any upset conditions. It is known that in those circumstances, emissions increase and additional decomposition products from the plastic melt are expected (6).

1. Experiments with Polystyrene

Table V summarizes the percentage organic emission of PS in four plastic processes. The analysis were conducted with GC/MS procedures. The organic vapors were collected with a Carbotrap 300 tube which is specifically recommended for identification of aromatic organic compounds. The procedures detailed in the methods sections were followed. Sample collection locations are described in Figures 1 to 5 in Appendix A. The highest emission detected in these experiments was styrene, followed by its dimers and trimers, as well as other aromatics. The only non-aromatic compounds detected were benzaldehyde and acetophenone. The footnotes of the table should be taken into consideration to interpret the results.

The results of these experiment for polystyrene (Tables V, XII, XIII) confirm earlier European and U.S. studies where styrene and aerosols were the highest relative emissions

from thermal degradation of PS (7)(10).

2. Experiments with Polyethylene

Three different sets of experiments were conducted to identify polyethylene (PE) emissions. In the first set, emissions were collected in **Carbotrap** tubes for desorption and analysis by GC/MS. The objective was to identify aliphatic compounds. The second set was planned to collect aldehydes and other oxygenated compounds. Emissions were collected in impingers containing di-nitro phenyl hydrazone and analyzed by HPLC/UV. This method is specific for aldehydes and ketones. The third set was planned to collect organic acids by collecting emissions in a silica gel tube, followed by HPLC/UV analysis.

a) Organic Vapors Analyzed by GC/MS

Table VI summarizes the percentage of relative organic emission of PE in three processes. The first column shows the emission percentages of an extrusion paper coating operation. Molten PE from an extruder was coated onto a moving paper roll. A preliminary experiment using a **Carbotrap 300** collection tube emitted complex organics that were detected as "unknown aromatics" in the GC/MS analysis. These results were interpreted as contaminants generated from the paper being coated. It was also observed that the detection tube (**Carbotrap 300**), which is designed to collect aromatic organics, might have failed to capture aliphatic polar organics. It is known from the literature that these later compounds are emitted from molten PE (12).

Based on these observations, the experiment was repeated extruding PE under coating conditions, but removing the paper roll and using a sample collector tube (**Carbotrap 200**) specifically designed to collect aliphatic organics. The objective of the

changes was twofold: to collect aliphatic organic emissions missed in the preliminary experiment in the **Carbotrap 200** tube, and to avoid any contaminant originated from the paper in the coating operation.

The results with the **Carbotrap 200** tube identified a high percentage of aldehydes and other polar compounds absent in the preliminary experiment. The results are shown in the first column of Table VI. These results prompted a second sampling campaign to quantitatively measure the aldehydes generated in PE extrusion for paper coating.

The emissions evaluated from the two other PE processes (LLDPE Blown Film and HDPE Injection molding) were also collected in **Carbotrap 200** tubes. The percentages of organics emitted appear in Table VI.

The results of this experiment confirm earlier European studies where oxygenated compounds were the highest emissions from thermal degradation of PE (10).

b) Aldehydes analyzed by HPLC/UV

Table VII summarizes the mass percentage of the emissions of aldehydes from the extrusion paper coating processes previously studied (LLDPE Paper Coating, Table VI, first column). Identical machines, materials, temperatures and sampling conditions as in the first experiment were used. The aldehydes in this table were individually determined with their specific calibration factor. HPLC/UV was used in this experiment to quantitatively measure each aldehyde generated from the PE melt. Results appear in Table VII. The high generation of formaldehyde confirms previous PE emission studies (4), (11).

c) Organic Acids analyzed by HPLC/UV

Table VIII summarizes the mass percentage of the emissions of organic acids

generated from the PE melt. HPLC was used as the analytical technique, since it is more suited for organic acid detection (16). The analytical details appear in Appendix D. The only organic acid above the detection limit of the method was formic acid. It has been suggested (3) that some of the organic acids reported in previous studies (11) might be direct products of oxidation of the high levels of aldehyde emissions generated.

3. Experiments with Acrylonitrile-butadiene-styrene (ABS)

Table IX summarizes the mass percentage of the relative emissions generated from three processes using ABS as the raw material. Since the emissions expected were aromatic organic chemicals, the collection tube was a **Carbotrap 300** and vapors were analyzed by GC/MS, as described in the methods section. The principal emissions were styrene, acrylonitrile and some benzene derivatives. The presence of acrylonitrile is confirmed from previous reports (16).

4. Experiments with Polyvinyl Chloride

Table X summarizes the mass percentage of the relative emissions generated from three processes where PVC was used as raw material. **Carbotrap 200** collection tubes were used since polar aliphatic compounds were expected. The organic vapors were analyzed by GC/MS in the usual manner described in the materials and methods section. Very small amounts of emissions were detected in these sets of experiments. Only the extrusion process generated significant emissions. However, is not clear if the emissions are from the polymer itself or the additives in the plastic. Vinyl chloride was not detected under the conditions of these experiments. The detection limit for GC/MS was 0.001ugm.

Samples were collected and analyzed for hydrochloric acid during the three

experiments. The collection media used was silica gel tubes and the analysis was performed by Ion Chromatography (**NIOSH Method 7903**). All the samples reported levels below the detection limits.

Lead aerosol samples were also collected during the three experiments and analyzed by Atomic Absorption Spectrophotometry (AA) (**NIOSH Method 7082**). The samples were below detection limits of the method (>O.OO1 ugm).

5. Experiments with Compression Molding of (BMC)

Table XI summarizes the mass percentage of the relative emissions generated during mixing of materials and compression molding of a thermoset polyester formulation. The recipe included: a thermoset resin, styrene, calcium stearate and carbonate, glass fibers and catalyst. **Carbotrap 300** tubes were used since aromatic organic emissions were expected. The collected organic vapors were analyzed by GC/MS. The process of MS analysis was changed slightly by the introduction of 3 additional calibrating substances for the MS quantification procedure (toluene, chlorobenzene, dicholoro ethylene, as well as the original calibrating substance: benzene). The only significant emission was styrene for both mixing and molding.

C. Aerosol Emissions by Polymer

1. Total Aerosol Emissions

Generation of polymer aerosol emissions (i.e., solid condensates of organic products) was observed in various processes with different polymers. The results are summarized in Table XII. The gravimetric sampling procedure (**NIOSH Method 0500**) used requires that the filters collected be desiccated for 24 hours previous to weighing. Therefore, any

volatiles captured in the filter evaporate before the weighing procedure. The generation of particulate emissions was confirmed from past experimental reports (3), (6), (9). PS, PE and ABS seem to generate measurable amounts of aerosols, as shown in the results.

2. Benzene Soluble Aerosols

Table XIII summarizes the results of emissions of aerosols reported as the weight of organics extracted from the filter with benzene. The methodology of sampling and analysis permits the inclusion of condensate vapors in the gravimetric analysis in addition to the solid aerosols. Since the sampling cassettes for this collection and analysis method are sealed and there was not a desiccation process before weighing, the results in the table include both solid aerosols and condensate organics. The method used was **NIOSH Method 5023.**

IV. CONCLUSIONS

The principal objective of these experiments was to identify the best collection and analytical techniques available to conduct **source sampling** during plastics processing, and use them to prepare sampling protocols. Source samples of emissions from polymers in various processes were obtained in order to choose a set of **target substances** that would be representative of emissions in industrial settings. Preliminary sampling protocols for source emission identification were developed for five commercial plastics in seven plastics processes. The study of previously published reports and the detection of emissions from seven plastic processes and five polymers permitted a reasonable basis to choose the **target substances**. The target substances chosen from these experiments are identified in Table XIV. The focus of the project was to *identify* emissions generated by the melting of the polymers per se during steady state operations. Emissions originated by additives or during non-steady state operations are beyond the scope of this study.

The continuation of this project will permit the development of specific sampling protocols that will allow for a more accurate measurement of the emissions of the target substances identified here.

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Table I

Characteristics of Plastics Process Machinery at University of Massachusetts-Lowell Plastics Engineering Department			
Process	Machinery	Model	Material
Extrusion[1] Strand Die	Welex	24:1 L/D 2 inch Dia.	PS, ABS, PVC
Extrusion[1] Sheet Die	Modern Plastic Mach.	150.20 Die Width 15"	PS, ABS
Extrusion[1] Paper-coating	Modern Plastic Mach.	20:1 L/D 1.5 inch Dia.	PE (LLDPE)
Extrusion[1] Blown-Film	Blown Film MPM	VEXCL 028	PE (LLDPE)
Injection Molding [2]	Battenfeld	BA 750	PS, ABS, PE(HDPE), PVC
Thermoforming[2]	Comet Lab. Thermoformer	1424 Sheet Fed	PS, PVC, UP(BMC)
Compounding [2]	Baker Perkins	Sigma Blade Mixer	UP(BMC)

Notes on Table I:

1 = All extruders are one stage.

2 = Machines equipped with local exhaust ventilation (LEV). The remaining machines under general exhaust ventilation (GEV).

PS = Polystyrene

PE = Polyethylene

LLDPE = Linear low density polyethylene

HDPE = High density polyethylene

ABS = Acrylonitrile-butadiene-styrene

PVC = Polyvinyl chloride

UP(BMC) = Unsaturated Polyester (Bulk Molding Compound)

VI. TABLES

Table II

Plastic Raw Materials used in Process Emissions Experiments				
Extrusion Processes				
	Strand	Sheet	Blown Film	Paper Coat
Polystyrene	General Purpose PS Extr. Grade	General Purpose PS Extr. Grade		
Polyethylene			LLDPE Extr. Grade	LLDPE Extr. Grade
ABS	ABS Extr. Grade	ABS Extr. Grade		
PVC	Flexible PVC Extr. Grade			
Injection Molding Thermoforming and Bulk Molding				
	Injection	Thermoforming	Molding	Mixing
Polystyrene	Gen. Purp. PS Injec. Grade	Gen. Purp. PS Sheet*		
Polyethylene	HDPE Injec. Grade			
ABS	ABS Injec. Grade			
UP(BMC)			High Temp.# UP-styrene	High Temp.# UP-styrene
PVC	Rigid PVC Injec. Grade	Gen. Purp. Crystal PVC		

Notes on Table II:

All the plastics are commercial chemical products containing a variety of processing aids, impact modifiers, fillers, plasticizers, lubricants and pigments. Some or all of these additives can volatilize during the melting process.

* = PS Sheet commercially available, not extruded at UMass Lowell.

\# = Microwave cookware resin formulation.

TABLE III

Selected* Process Emissions Identified by Air Sampling
(Analysis by GC/MS, HPLC/UV, Ion Chromatography)

EXTRUSION PROCESSES				
	Strand	Sheet	Blown Film	Extr. Coating
PS	Styrene Styrene Dimer Ethylbenzene Toluene Benzaldehyde Acetophenone Benzene	Styrene Styrene Dimer Styrene Trimer Ethylbenzene Toluene Benzaldehyde Acetophenone Benzene		
PE			Trimethyl-pentane Xylene Ethylhexane Trimethyl-hexane Octene Decane Benzene (Toluene)[1] (Ethylbenzene)[1]	Formaldehyde+ Acetaldehyde+ Propional+ Valeraldehyde+ Acrolein+ Formic Acid& Benzene Xylene (3) Trimethyl- C_4H_{10}, C_5H_{12}, C_6H_{14} (3) Alkanes C_8, C_9, C_{10}

	Strand	Sheet	Blown Film	Extr. Coating
ABS	Acrylonitrile Styrene Toluene Cumene Benzaldehyde Propylbenzene Ethylbenzene SAN Dimer Styrene Dimer Phenol Subst. Nitrogenated compounds	SAN Dimer Styrene Toluene Cumene Benzaldehyde Propylbenzene Xylene Acrylonitrile Styrene Dimer Phenol Subst. Nitrogenated compounds		
PVC	Octadecane Nonanol Oxirene Styrene Cyclopropane Dimethyl-pentanol Xylenes Benzene			

Notes on Table III

* = The compounds selected for this table were positively identified and were present at levels 10X the analytical detection limit (>0.001 ug for GC/MS). **Some of the organic chemicals could have been originated from the additives in the plastics used as raw materials.** Unless otherwise noted, all compounds analyzed by GC/MS were collected in **Carbotrap 300** or **200** adsorption tubes (all collection tubes were **Carbotrap 300** except for Polyethylene/Paper Coating and PVC experiments where **Carbotrap 200** was used). Collection was followed by thermo-desorption and the samples were analyzed by Gas Chromatography (GC) for separation and Mass Spectrometry (MS) for identification and relative quantification. The analytical procedure used was **EPA Method 624**. Exceptions to this method are listed below.

\+ = Samples collected in two bubblers in series with a solution of DNPH and iso-octane. Analysis was performed by HPLC/UV. **EPA Method TO-5.**

Notes on Table III Continuation:

& = Samples collected on silica gel tubes and analyzed by HPLC/UV.

1 = Emissions of Toluene and Ethylbenzene in Blown film were unexplained, since they are not expected to be generated by the polymer. It is possible that could be generated by additives or laboratory contamination.

PS = Polystyrene

PE = Polyethylene

ABS = Acrylonitrile-butadiene-styrene

SAN = Styrene-acrylonitrile co-polymer.

TABLE IV

Selected* Process Emissions Identified by Air Sampling
Analysis Performed by GC/MS

INJECTION MOLDING AND THERMOFORMING				
	Injection	Thermoforming	Bulk Molding	Compounding
PS	Xylene Isomers Ethylbenzene Toluene	Styrene Toluene Benzaldehyde Xylene Isomers		
PE	Tetramethyl-butane Alkanes > C_9 (Toluene)[1] (Ethylbenzene)[1]			
ABS	Styrene Xylene Toluene Ethylbenzene Tri-methyl-decane Isomer Naphthalene-carbo-nitrile			
UP BMC			Styrene $(CH_3)_4$-butane $(CH_3)_4$-decane Benzaldehyde Propyl benzene	Styrene Dimethyl-nonane Trimethyl-decane
PVC	Toluene Styrene Benzene Octanol Octacosane Dimethyl-undecane Ethylbenzene Xylenes	Oxirene Toluene Ethyl-hexyl-acetic acid Benzaldehyde $(CH_3)_3$-decane Xylenes		

See notes on Table IV on next page:

Notes on Table IV

•	=	The compounds selected for this table were positively identified and were present at levels 10X the analytical detection limit (>0.001 ug for GC/MS). **Some of the organic compounds could have originated from the additives present in each plastic.** Unless otherwise noted, all the emissions were collected using a Carbotrap 300 tube. Collection was followed by thermo-desorption and the samples were analyzed by Gas Chromatography and Mass Spectrometry (GC/MS). The analytic procedures used were **EPA Methods 624 and 8240. Carbotrap 300** tubes were used to collect organic vapors for PS and ABS. **Carbotrap 200** tubes were used for PE and PVC.
1	=	Emissions of Toluene and Ethylbenzene in Injection Molding of PE were unexplained, since they are not expected to be generated by the polymer. It is possible that could be generated by additives or laboratory contamination.
PS	=	Polystyrene
PE	=	Polyethylene
ABS	=	Acrylonitrile-butadiene-styrene
PVC	=	Polyvinyl chloride
UP	=	Unsaturated polyester (Bulk Molding Compound)

Table V

Mass Percentages of Vapors Collected Based on Amounts of Selected[1] Emissions of Polystyrene				
	Extrusion Strand	Extrusion Sheet	Inj. Mold.	Thermfm.
Steady State Mat. Flow-Rate (kg/hr)	10.4	5.3	4.0	2.6
Highest Operating Temperature (°F)	445	466	440	220
Effluents Identified	%	%	%	%
Styrene	50	66	45.8	48
Styrene Dimer	38	5.3	12.5	ND
Styrene Trimer	ND	15	ND	ND
Ethylbenzene	1.5	3	ND	1
Propylbenzene	0.5	0.3	16.7	ND
Acetophenone	0.5	*	ND	ND
Toluene	0.4	0.6	4.2	4
Benzaldehyde	0.2	2	ND	5
Benzene	*	*	4.2	ND
Xylene Isomers	ND	*	16.7	2
Total % Selected[1] Organics Quantified	91	92	100	60
% Not Quantified Organics	9	8	0	40

Notes on Table V see next page:

Notes on Table V:

The absolute amounts of organic emissions collected varied widely depending on the process. They ranged from total organics collected of 0.02 to 85 ugm depending on the circumstances of the different processes. Therefore it is not possible to compare the percentages generated between processes, i.e., between columns.

1 = The compounds selected for this table were positively identified and were present at levels 10X the analytical detection limit of the GC/MS (>0.001 ugm). Background organic vapors in the laboratory air were subtracted from the concentrations found in the sample. The collection tube for all experiments was Carbotrap 300.

ND = Not Detected

* = Identified but not accurate quantification could be made because of the very small amount of the organic vapor collected from the process.

Table VI

Mass Percentages of Vapors Collected Based on Amounts of Selected[1] Emissions of Polyethylene			
	LLDPE[2] Extrusion	LLDPE Blown Film	HDPE Injec. Molding
Steady State Material Flow-Rate (kg/hr)	3.48	2.48	2.64
Highest Operating Temperature (°F)	620	500	450
Effluents Identified	%	%	%
Benzene	ND	0.4	ND
Tetra-Methylbutane	2.1	ND	14.3
Xylene Isomers	ND	9.4	ND
Trimethyl-Pentane	8.0	16.3	ND
Trimethyl-Hexane	5.7	6.5	ND
Ethyl-Hexane	ND	7.7	ND
Decane Isomers	14.8	4.5	ND
Nonane Isomers	7.4	ND	*
Octane Isomers	17.1	3.3	ND
Unknown Alkanes	7.2	1.2	42.8
Unknown Aldehydes	30.2	ND	ND
Total % Selected[1] Organics Quantified	92.6	85.8@	100@
% Organics not Quantified	7.4	14.2	0.0
% Toluene[3]	ND	19.1	28.6
% Ethylbenzene[3]	ND	17.5	14.3

For Notes on Table VI see next page.

Notes on Table VI

1 = The compounds selected for this table were positively identified and were present at levels 10X the analytical detection limit of the GC/MS (>0.001 ugm). Background organic vapors in the laboratory air were substracted from the concentrations found in the sample. The collection tube for all experiments was **Carbotrap 200**. The procedure used was EPA Method 624.

2 = Polyethylene was extruded in a paper-coating operation but the paper was eliminated to avoid vapors that could be generated by the heating of the paper. Vapors were collected on a **Carbotrap 200** tube. The tube was then thermo-desorbed and analyzed by **GC/MS.**

3 = Emissions of Toluene and Ethylbenzene in the Blown film and Injection Molding experiments were unexplained since they are not expected to be generated by the polymer. It is possible that these two compounds could have been generated by additives or laboratory contamination.

ND = Not Detected

@ = Toluene and Ethylbenzene included in the total % of quantified organic emissions

LLDP = Linear low density polyethylene

HDPE = High density polyethylene

• = Identified but not accurate quantification could be made because of the very small amount of the organic vapor collected from the process.

Table VII

Mass Percentages of Aldehydes[1] from Extruded Polyethylene		
	LLDPE[2] Extrusion Paper-Coating	LLDPE[3] Extrusion No-Paper
Steady State Material Flow-Rate (kg/hr)	3.48	3.48
Highest Operating Temperature (°F)	617	620
Aldehydes Identified	%	%
Formaldehyde	27.50	44.00
Acetaldehyde	30.00	34.66
Acrolein	6.00	5.34
Propionaldehyde	12.50	16.00
Valeraldehyde	24.00	ND
Total % Aldehydes + Quantified	100.00	100.00

Notes on Table VII

1 = Aldehydes were collected and analyzed by EPA Method TO-5. Vapors are collected in a solution of iso-octane and di-nitrophenyl hydrazone (DNPH) contained in two bubblers in series. The solution was analyzed by HPLC/UV.

2 = Polyethylene was extruded in a paper-coating operation. Vapors for aldehyde analysis were collected in two bubblers in series, as described above. The sample probe was placed at the point were the hot PE sheet met the paper roll near the exit of the die.

Notes on Table VII (continuation):

3 = Polyethylene was extruded in a paper-coating operation in an identical set-up from the previous experiment but no paper was used. The sample probe was placed at the point were the hot PE sheet was exiting from the die.

+ = Other aldehydes and ketones were also present at concentrations below the detection limits of the analytical method (v.g.: acetone, crotonaldehyde, isobutyraldehyde, methyl-ethyl-ketone and benzaldehyde.

ND = Not Detected

Table VIII

Mass Percentages of Organic Acids[1] from Extruded Polyethylene	
	LLDPE[2] Extrusion
Steady State Material Flow-Rate (kg/hr)	3.48
Temperature (°F)	620
Sampling Time (minutes)	60
Organic Acids Analyzed by HPLC	%
Acetic Acid	ND
Formic Acid	100
Acrylic Acid	ND
Total % Organic Acid Quantified	100

Notes on Table VIII:

1 = Organic Acids were collected and analyzed by a modified OSHA-38 method for organic acids. Vapors were collected in a silica gel collection tube. The sample was then desorbed in a methanol solution and analyzed by HPLC/UV.

2 = Polyethylene was extruded in a paper-coating operation whithout paper.

\+ = Other organic acids were also present at concentrations below the detection limits of the analytical method (e.g.: acetic acid and acrylic acid).

ND = Below the detection limits of the collection and analytical method.

Table IX

Mass Percentages of Vapors Collected Based on Amounts of Selelected[1] ABS Organic Emissions			
	Extrusion Strand	Extrusion Sheet	Inj. Mold
Steady State Mat. Flow-Rate (kg/hr)	8.40	6.22	0.946
Highest Operating Temperature (F)	450	450	460
Effluents Identified	%	%	%
Acrylonitrile	0.3	ND	ND
Styrene	21.9	18.4	ND
Styrene dimer	1.5	0.7	ND
Unknown styrenic	3.5	1.9	ND
SAN dimer	0.5	0.1	ND
Alpha-methyl styrene	ND	1.3	ND
Xylene isomer	0.5	10.5	4.9
Styrene/Xylene isomer	ND	ND	35.2
C_4-Benzene isomer	ND	6.9	ND
C_5-Benzene isomer	2.8	1.1	ND
Ethyl Benzene	4.2	ND	3.4
Methyl(methyl-ethenyl) benzene isomer	5.1	ND	ND
$C_{10}H_{16}$ isomer	ND	15.8	ND
Substituted phenol	23.5	7.5	ND
Trimethyl bicyclo-heptanol	3.4	2.4	ND
Trimethyl decane isomer	ND	ND	9.3

Trimethyl bicyclo-heptane	5.0	3.0	ND
2,6-Bis (Dimethylethyl) methyl Phenol isomer	4.4	ND	ND
Toluene	2.7	2.5	16.7
Cumene	3.0	2.1	1.9
Benzaldehyde	1.8	ND	10.5
n-propyl benzene	1.6	1.0	ND
Unknown nitrogen compound	7.0	5.4	ND
Dichlorobenzene*	ND	ND	9.6
Unknown C_{16} Alcohol	ND	3.2	ND
Total % Selected[1] Oraganics Quantified	92.4	83.8	91.4
% Organics not Identified	7.6	16.2	8.60

Notes on Table IX:

1 = The compounds selected for this table were positively identified and were present at levels 10X the analytical detection limit of the GC/MS (>0.001 ugm). Background organic vapors in the laboratory air were substracted from the concentrations found in the sample. The collection tube for all experiments was Carbotrap 300. The procedure used was EPA Method 624.

ND = Not Detected

* = Possibly generated from additives

Table X

Mass Percentages of Vapors Collected Based on Amounts of Selected[1] PVC Organics			
	Extrusion Strand	Thermoforming	Injection Molding
Steady State Material Flow Rate (kg/hr)	15	3.48	0.5
Highest Operating Temperature (°F)	355	320	400
Effluents Identified	%	%	%
Benzaldehyde	nd	6.2	nd
Trimethyldecane	nd	2.5	nd
Acetic Acid-ethyl hexyl ester	nd	14.9	nd
Benzene	0.4	2.5	5.4
Ethylbenzene	0.1	1.3	•
Tetrachloroethylene	nd	0.2	nd
Toluene	nd	17.4	39.5
Xylenes (total)	0.1	3.7	1.5
1-Octanol	nd	nd	11.5
Decane,2,9-Dimethyl	nd	nd	3.7
Undecane,2,10-Dimethyl	nd	nd	4.8
Octacosane	nd	nd	4.0
Styrene	0.5	nd	26.5
Trichloroethylene	•	nd	1.0
Oxirane {(2-Ethyl Hexyl) oxy) Methyl)}	8.4	51.0	nd
1-Pentanol,2,3, Dimethyl	0.3	nd	nd

Cyclopropane, Pentanol	18.7	nd	nd
1-Nonanol	17.3	nd	nd
5-Octadecane	23.5	nd	nd
9-Octadecane	26.2	nd	nd
1-Hexadecane	4.4	nd	nd
Total % Selected[1] Organics Quantified	99.9	99.7	97.9
% Organics not Identified	0.1	0.3	2.1

Notes to Table X:

1 = The compounds selected for this table were positively identified and were present at levels 10X the analytical detection limit of the GC/MS (>0.001 ugm). Background organic vapors in the laboratory air were substracted from the concentrations found in the sample. The collection tube used for all experiments was **Carbotrap 300**.

nd = Not Detected

• = Compound identified but no accurate quantification could be made because of the very small amount of the organic vapor collected from the process.

Table XI

Mass Percentages of Vapors Collected Based on Amounts of Selected[1] Emissions of Polyesters (BMC)		
	Compression Molding	Material Mixing
Material Flow (kg/Cycle)	1.50	1.50
Highest Operating Temperature (°F)	270	270
Effluents Identified	%	%
Styrene	97.5	91.8
Dimethyl-nonane	nd	2.2
Tri-methyl-decane	0.3	1.6
Tetra-methyl-butane	1.8	nd
Isopropyl-benzene	*	nd
Benzaldehyde	0.3	nd
Total % of Selected[1] Organica Quantified	99.9	95.6
% Organics not Quantified	0.1	4.4

Notes on Table XI:

1 = The compounds selected for this table were positively identified and were present at levels 10X the analytical detection limit of the GC/MS (>0.001 ugm). Background organic vapors in the laboratory air were substracted from the concentrations found in the sample. The collection tube used for all experiments was **Carbotrap 300.**

nd = Not Detected

* = Compound identified but no accurate quantification could be made because of the very small amount of the organic vapor collected from the process.

Table XII

Aerosol Concentrations in mg/m^3 (Total Particulate) Measured during Process Emissions Experiments				
Extrusion Processes				
	Strand	Sheet	Blow Film	Paper Coating
Polystyrene	14.00	1.12	-	-
Polyethylene	-	-	0.48	5.19
ABS	7.66	1.79	-	-
PVC	ND	-	-	-

Injection Molding and Thermoforming				
	Injection	Thermoforming	BMC	Mixing (BMC)
Polystyrene	0.41	ND	-	-
Polyethylene	ND	-	-	-
ABS	ND	-	-	-
Polyester	-	-	ND	ND
PVC	ND	ND	-	-

Notes on Table XII:

Samples were collected in a tared 37-mm, 5um PVC filter for one hour at 2 L/minute. The filters were weighed in an exact balance with a 0.01 mg sensitivity. This method is **NIOSH Method 0500 .**

ND = Sampled but non detected.

\- = Not sampled, experiment not run.

Table XIII

Benzene Soluble Particulate Concentrations in mg/m^3 Measured during Process Emissions Experiments				
Extrusion Processes				
	Strand	Sheet	Blown Film	Paper Coating
Polystyrene	6.32	0.08	-	-
Polyethylene	-	-	5.58	7.56
ABS	31.91	20.30	-	-
PVC	ND	-	-	-
Injection Molding and Thermoforming				
	Injection	Thermoforming	BMC	Mixing (BMC)
Polystyrene	0.17	ND	-	-
Polyethylene	ND	-	-	-
ABS	ND	-	-	-
Polyester	-	ND	ND	ND
PVC	ND	ND	-	-

Notes on Table XIII:

Samples were collected in a tared 37-mm, 2um PTFE membrane filter for one hour at a sampling rate of 2 L/minute. The filters without desiccation were extracted with benzene and weighed in an exact balance with a 0.01 mg sensitivity. This is NIOSH Method 5023.

ND = Sampled but not detected.

- = Not sampled, experiment not run.

Table XIV

Recommended Target Substances Generated During Steady State Plastic Processes Experiments	
Plastic	Target Substance
Polystyrene[1]	Styrene, Ethylbenzene, Toluene, Benzene[3]
Polyethylene[1]	Formaldehyde, Formic Acid Benzene[3]
ABS[1]	Styrene, Xylene Toluene, Acrylonitrile
PVC	Vinyl Chloride[2], Hydrochloric Acid[2] Benzene[3], Toluene
BMC	Styrene

Note on Table XIV:

1 = Polystyrene, Acrylonitrile-butadiene-styrene (ABS) and Polyethylene generate solid condensation particulate during process melting. Total Particulate sampling is also recommended for these plastics as an indicator of emissions.

2 = Not detected in these experiments but recommended as target substance because of regulatory interest.

3 = Present in very small amounts but recommended as a target substance because of regulatory interest.

VII. APPENDIXES