

November 9, 1992

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FROM: M. M. Marshall *mm*

RE: U. MASS. LOWELL PROCESS EMISSIONS STUDY

The final report from U. Mass. Lowell to SPI was distributed to OHEIC (Occupational Health and Environmental Issues Committee) members at the November 6 meeting. Unfortunately, an extensive rewriting was required to the original submittal on July 18, which has taken several weeks. The report will be issued to SPI member companies by the end of the year with a cover letter to be drafted by David Sarvadi of Keller & Heckman containing several caveats.

It should be noted that the data was obtained only after the processes reached steady state operation and the authors feel that "the emissions were at the peak off-gassing stage of the plastic production cycle" under the specific conditions described in the report. PVC products were provided by Geon: flexible PVC extrusion grade, rigid PVC injection grade and general purpose crystal PVC used in the thermoforming operation. Mass percentages of vapors collected during PVC processing are listed in tables X, p. 42 & 43; XII, p. 45; XIII, p. 46 and XIV, p. 47. As stated in the draft report, which was previously distributed, VCM and HCl were not detected and benzene was "present in very small amounts".

The major ABS producers are very dissatisfied with this study and have funded any independent study by Battelle. A group of polyethylene producers plan to do the same and Dow is also considering commissioning Battelle to do a study on polystyrene. However, U. Mass. Lowell has the right to (and almost certainly will) publish this study. By copy of this memo, I am requesting Bob Burnett to have it reviewed by the appropriate Vinyl Institute Committees. Please do not release the report or any of the data outside of GVD until I give the "green light".

cc: Bob Burnett

UMASS.MMM

25285001

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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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 cm³/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 μ m 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 cm³/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 μgm) 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.