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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.

BY:

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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

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/m³ (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.

APPENDIX C

Analytical Methods for

1. Organic Vapors EPA - 624 (8240 A)

2. Aldehydes EPA - TO 5

3. Organic Acids OSHA - 38
   (as Acrylic Acid) Dow Chemical Modifications

4. Aerosol Sampling

   * Total Dust NIOSH - 0600

   * Benzene Soluble
     Particulate NIOSH - 5023

   * Lead NIOSH - 7082

5. Inorganic Acids
   Hydrochloric Acid NIOSH - 7903

TABLE 7.
METHOD ACCURACY AND PRECISION AS FUNCTIONS OF CONCENTRATION[a]

Parameter	Accuracy, as recovery, x' (µg/L)	Single analyst precision, s_r' (µg/L)	Overall precision, S' (µg/L)
Benzene	0.93C+2.00	0.26$\bar{x}$-1.74	0.25$\bar{x}$-1.33
Bromodichloromethane	1.03C-1.58	0.15$\bar{x}$+0.59	0.20$\bar{x}$+1.13
Bromoform	1.18C-2.35	0.12$\bar{x}$+0.34	0.17$\bar{x}$+1.38
Bromomethane	1.00C	0.43$\bar{x}$	0.58$\bar{x}$
Carbon tetrachloride	1.10C-1.68	0.12$\bar{x}$+0.25	0.11$\bar{x}$+0.37
Chlorobenzene	0.98C+2.28	0.16$\bar{x}$-0.09	0.26$\bar{x}$-1.92
Chloroethane	1.18C+0.81	0.14$\bar{x}$+2.78	0.29$\bar{x}$+1.75
2-Chloroethylvinyl ether[a]	1.00C	0.62$\bar{x}$	0.84$\bar{x}$
Chloroform	0.93C+0.33	0.16$\bar{x}$+0.22	0.18$\bar{x}$+0.16
Chloromethane	1.03C-1.81	0.37$\bar{x}$+2.14	0.58$\bar{x}$+0.43
Dibromochloromethane	1.01C-0.03	0.17$\bar{x}$-0.18	0.17$\bar{x}$+0.49
1,2-Dichlorobenzene[b]	0.94C+4.47	0.22$\bar{x}$-1.45	0.30$\bar{x}$-1.20
1,3-Dichlorobenzene	1.06C+1.68	0.14$\bar{x}$-0.48	0.18$\bar{x}$-0.82
1,4-Dichlorobenzene[b]	0.94C+4.47	0.22$\bar{x}$-1.45	0.30$\bar{x}$-1.20
1,1-Dichloroethane	1.05C+0.36	0.13$\bar{x}$-0.05	0.16$\bar{x}$+0.47
1,2-Dichloroethane	1.02C+0.45	0.17$\bar{x}$-0.32	0.21$\bar{x}$-0.38
1,1-Dichloroethene	1.12C+0.61	0.17$\bar{x}$+1.06	0.43$\bar{x}$-0.22
trans-1,2,-Dichloroethene	1.05C+0.03	0.14$\bar{x}$+0.09	0.19$\bar{x}$+0.17
1,2-Dichloropropane[a]	1.00C	0.33$\bar{x}$	0.45$\bar{x}$
cis-1,3-Dichloropropene[a]	1.00C	0.38$\bar{x}$	0.52$\bar{x}$
trans-1,3-Dichloropropene[a]	1.00C	0.25$\bar{x}$	0.34$\bar{x}$
Ethyl benzene	0.98C+2.48	0.14$\bar{x}$+1.00	0.26$\bar{x}$-1.72
Methylene chloride	0.87C+1.88	0.15$\bar{x}$+1.07	0.32$\bar{x}$+4.00
1,1,2,2-Tetrachloroethane	0.93C+1.76	0.16$\bar{x}$+0.69	0.20$\bar{x}$+0.41
Tetrachloroethene	1.06C+0.60	0.13$\bar{x}$-0.18	0.16$\bar{x}$-0.45
Toluene	0.98C+2.03	0.15$\bar{x}$-0.71	0.22$\bar{x}$-1.71
1,1,1-Trichloroethane	1.06C+0.73	0.12$\bar{x}$-0.15	0.21$\bar{x}$-0.39
1,1,2-Trichloroethane	0.95C+1.71	0.14$\bar{x}$+0.02	0.18$\bar{x}$+0.00
Trichloroethene	1.04C+2.27	0.13$\bar{x}$+0.36	0.12$\bar{x}$+0.59
Trichlorofluoromethane	0.99C+0.39	0.33$\bar{x}$-1.48	0.34$\bar{x}$-0.39
Vinyl chloride	1.00C	0.48$\bar{x}$	0.65$\bar{x}$

x' = Expected recovery for one or more measurements of a sample containing a concentration of C, in µg/L.

s_r' = Expected single analyst standard deviation of measurements at an average concentration of $\bar{x}$, in µg/L.

S' = Expected interlaboratory standard deviation of measurements at an average concentration found of $\bar{x}$, in µg/L.

C = True value for the concentration, in µg/L.

$\bar{x}$ = Average recovery found for measurements of samples containing a concentration of C, in µg/L.

a Estimates based upon the performance in a single laboratory.

b Due to chromatographic resolution problems, performance statements for these isomers are based upon the sums of their concentrations.