

Casting Emission Reduction Program



Operated by

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Mold Making Emissions from the ProMetal S15 **Digital Printing Machine**

1412-124 HRa

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Mold Making Emissions from the ProMetal S15 Digital Printing Machine

1412-124 HRa

This report has been reviewed for completeness and accuracy and approved for release by the following:

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Date

The data contained in this report were developed to assess the relative emissions profile of the product or process being evaluated. You may not obtain the same results in your facility. Data were not collected to assess cost or producibility.

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TABLE OF CONTENTS

Executive	Summary1
1.0	Introduction
1.2.	CERP/Technikon Objectives
1.3.	Report Organization
1.4.	Specific Test Plan and Objectives
2.0	Test Methods, Assumptions and Procedures5
2.1.	Description of Process and Testing Equipment
2.2.	Description of Testing Program
2.2	.2. Test Plan Review and Approval
2.2	.3. Data Reduction, Tabulation and Preliminary Report Preparation12
2.2	.4. Report Preparation and Review
2.3.	Quality Assurance and Quality Control (QA/QC) Procedures
3.0	Test Results15
3.1.	Discussion of Results
Appendix	A Test and Sample Plans and Process Instructions25
Appendix	B Detailed Digital Printing Process Parameters
Appendix	C Continuous Emission Charts43
Appendix	D Acronyms and Abbreviations

LIST OF FIGURES AND TABLES

Table 1-1	Test Plan Summary4
Figure 2-1	The RCT System
Figure 2-2	Liquid Transfer into RCT Machine
Figure 2-3	Digital Printing of Gear Pattern7
Figure 2-4	Test HRa CAD Drawing and Diagram of 4-on Gear Molds7
Figure 2-5	CAD Drawing of Cope, Drag and Gear
Table 2-1	Emission Sampling and Analytical Methods9
Figure 2-6	VOSTs Located on Digital Printing Machine Vent11
Figure 2-7	Schematic of Sampling Configuration
Table 3-1	Test HRa Emissions Results – lb per Sampling Event16
Table 3-2	Percent Difference Between Calculated and Measured Multiple Mold and Storage Events
Table 3-3	Test HRa Emissions Results – lb per hour of digital printing time
Figure 3-1	Order of Anticipated Increase in Emissions with Number of Mold and Storage Events, lbs per event
Figure 3-2	Mass Emission Rate, lb/hour of printing21
Figure 3-3	Total Ion Chromatogram of Run HRa00322
Table 3-4	Major Compounds from GC/MS Analysis23

EXECUTIVE SUMMARY

This report contains the results of Test HRa, an evaluation of the airborne emissions released during the continuous manufacture of 4-on gear molds made using a digital mold machine (Pro Metal S-15 machine made by The ExOne Company). The machine employs a print head, which moves across the sand surface in a manner similar to how an ink jet printer moves across a paper surface, to dose a furfuryl alcohol based binder onto a thin layer of silica sand in a pattern dictated by a CAD file. After the pattern is printed on the sand layer, the machine's build platform lowers a minimal distance, and another layer of sand is applied by the recoater. The next slice of the pattern geometry is then printed. This process is repeated until all the printed layers complete the three dimensional pattern geometry. For Test HRa, the print box contained four copes and four drags placed symmetrically side-by-side in the print box.

Emissions were collected for varying time periods corresponding to the production of one to four molds, which completed a full print box. Times ranged from a 1 hour storage period, to the 35 hours required to print a full box containing the 4 molds. A total of six emission samples were collected. Chemical identification included general GC/MS analysis, as well as speciated analysis for furfuryl alcohol, furfural, formaldehyde, and sulfur dioxide.

Emissions were calculated as lbs per sampling event, and lbs per hour of printing. Emissions calculated on a lb per binder or lb per sand basis were neither reproducible nor representative due to the complex nature of the digital printing process.

Emission results from the testing performed and described herein are not suitable for use as emission factors or for purposes other than evaluating the relative emission reductions associated with the use of alternative materials, equipment, or processes. The emissions measurements are unique to the specific castings produced, materials used, and testing methodology associated with these tests. These measurements should not be used as the basis for estimating emissions from actual commercial foundry applications. this page intentionally left blank

1.0 INTRODUCTION

1.1. Background

Technikon, LLC is a privately held contract research organization located in McClellan, California, a suburb of Sacramento. Technikon offers emissions research services to industrial and government clients specializing in the metal casting and point source emissions areas. Technikon operates the Casting Emission Reduction Program (CERP). CERP is a cooperative initiative between the Department of Defense (US Army) and the United States Council for Automotive Research (USCAR). The parties to the CERP Cooperative Research and Development Agreement (CRADA) include The Environmental Leadership Council of USCAR, a Michigan partnership of DaimlerChrysler Corporation, Ford Motor Company, and General Motors Corporation; the U.S. Army Research, Development, and Engineering Command (RDECOM-ARDEC); the American Foundry Society (AFS); and the Casting Industry Suppliers Association (CISA). The US Environmental Protection Agency (US EPA) and the California Air Resources Board (CARB) also have been participants in the CERP program and rely on CERP published reports for regulatory compliance data. All published reports are available on the CERP web site at <u>www.cerp-us.org</u>.

1.2. CERP/Technikon Objectives

The primary objective of CERP is to evaluate materials, equipment, and processes used in the production of metal castings. Technikon's facility was developed to evaluate alternative materials and production processes designed to achieve significant air emission reductions. The facility's principal testing arena is designed to measure airborne emissions from individually poured molds. This testing facility enables the repeatable collection and evaluation of airborne emissions and associated process data.

1.3. Report Organization

This report has been written to document the methodology and results of a specific test plan that was used to evaluate the airborne emissions from the digital printing process.

Section 2.0 of this report includes a summary of the methodologies used for data collection and analysis, procedures for emission calculations, QA/QC procedures, and data management and reduction methods. Specific data collected during this test are summarized in Section 3.0. Section 3.1 of this report contains a discussion of the results.

The raw data for this test series are archived at the Technikon facility.

1.4. Specific Test Plan and Objectives

Test HRa was designed to evaluate airborne emissions generated during the manufacture of 4-on gear molds using a digital printing machine.

Table 1-1 provides a summary of the test plan. The details of the approved test plan are included in Appendix A.

Test Plan Number	1412-124-HRa
Type of Process Tested	Digitally printed mold making and curing
Casting/Mold Type	4-on irregular gear
Sand System	Prometal FS001-EU sand, with Prometal RCT binder FB001-EU and Prometal RCT activator FC001-EU
Number of Molds Printed	4
Test Dates	6/21/07-6/22/07
Process Parameters Measured	Mold weight

Table 1-1Test Plan Summary

2.0 TEST METHODS, ASSUMPTIONS AND PROCEDURES

2.1. Description of Process and Testing Equipment

The Rapid Casting Technology (RCT) system from The ExOne Company is a systems approach to the manufacture of sand molds and cores without the construction of separate patterns or core boxes. Sand molds and cores are printed directly onto sand in a "job box". Job box dimensions are1500 mm long by 750 mm wide by 700 mm high. Printing is accomplished by means of 3-dimensional digital printing. Digital system control is conveyed through a process computer link, and information regarding the mold or core geometry to be printed is communicated by a CAD file of the pattern of choice. Because the pattern is printed directly onto the sand, complicated core and mold geometries are easily created. The RCT system uses conventional foundry sand, resin binder, and activator. An integrated material handling system transports the job box from the 3D printing process station by means of powered material conveyance equipment, to an unloading station where the molds and cores are removed. The RCT system is housed in a dedicated climate controlled room, where temperature and humidity are maintained at approximately 68°F and 40%, respectively. Figure 2-1 shows the RCT system and peripheral equipment located in the 40' x 40' enclosure.





Each liquid component of the RCT system, which includes the binder, cleaner, and activator, is contained in a mobile vessel which connects directly to the machine when needing to be replenished. Transfer of the liquids into the machine is via an integral pumping system. Figure 2-2 shows an example of the binder being added to the machine. Liquid waste, consisting predominately of cleaner and some binder, is extracted in a similar manner. Sand is introduced to the system via a vacuum that transfers the sand from the holding hopper to the mixing station.



The print head has 512 print jets which deposit a furfuryl alcohol-based binder onto a thin (0.28 mm) layer of sand which has been mixed with 0.32% Based on Sand (BOS) of a toluenesulfonic acid activator. Wherever the binder is deposited on the activated sand, it reacts to bind the sand grains. The area where the binder has been jetted has a light green color (as shown in Figure 2-3) that darkens upon curing. After the binder is deposited on the sand -- in the essentially 2-dimensional geometry dictated by the CAD file -- the build platform lowers 0.28mm and another layer of sand is applied by the recoater. This process is repeated until the printed layers build to complete the desired three dimensional pattern geometry. For this test, four copes and four drags with a 4-on irregular gear pattern were placed symmetrically side-by-side in the print box. The gear pattern being printed can easily be seen in Figure 2-3. The print head is also visible in the upper right hand corner of the photograph.



Figure 2-4a shows the CAD drawing illustrating the symmetrical layout of the four copes and four drags in the print box. Figure 2-4b shows the detailed CAD drawing of the gear pattern.



Figure 2-4 Test HRa CAD Drawing and Diagram of 4-on Gear Molds

Figure 2-5 shows the cope and drag, and the final gear shape, as rendered by the CAD drawing. Details for these are given in Appendix B.





2.2. Description of Testing Program

The testing program encompasses the foundry process and emissions testing, both of which are rigorously controlled. For digital printing, all relevant parameters are recorded by the process computer. They include: print resolution, material usage, layer time, recoating time, printing time, cleaning time, hardware dialog, idle time, cleaning completion time, error time, and printhead recovery time. The detail of the individual parameters under these headings, which is printed at the conclusion of the printing process, is included in this report in Appendix B. Measured stack parameters included stack temperature, pressure, volumetric flow rate, and moisture content. All parameters were maintained within prescribed ranges to ensure the reproducibility of the test runs.

Emission testing for hydrocarbons included several methods. Method 18 is one of the US Environmental Protection Agency's (EPA) promulgated reference methods for volatile organic compound (VOC) analysis. Method 18 is generally used to identify and/or measure

as many compounds as possible in order to calculate actual VOC emissions from other measurements (e.g. EPA Method 25 or 25A). The method is a guideline and a system of quality assurance (QA) checks for VOC analysis rather than a rigorous, explicit manual for sampling or analysis.

As described in the method, sampling can be conducted using a Volatile Organic Sampling Train (VOST), which was the technique used for sampling emissions during the tests described herein. A sample gas stream was extracted from the source and then routed using the train through tubes containing adsorbents, which are the collection materials upon which the organic analytes are deposited. Adsorption tube samples were collected and analyzed for several target compounds using specific collection and analysis procedures based on approved federal methods, including those of the EPA. Under Method 18, samples were collected for general analysis using GC/MS. Individual component analysis for target compounds was done using sampling and analytical methods based on federal reference methods shown in Table 2-1. The details of the specific testing procedures and their variance from the reference methods are included in the Technikon Standard Operating Procedures.

Measurement Parameter	Test Method [#]
Port Location	US EPA Method 1
Number of Traverse Points	US EPA Method 1
Gas Velocity and Temperature	US EPA Method 2
Gas Density and Molecular Weight	US EPA Method 3a
Gas Moisture	US EPA Method 4 (Gravimetric)
Target VOCs and HAPs	US EPA Methods TO17, TO11; NIOSH 2529, 2505
TGOC	US EPA Method 25A

Table 2-1Emission Sampling and Analytical Methods

[#]Some methods modified to meet specific CERP test objectives.

TGOC as Propane was employed to measure undifferentiated hydrocarbon emissions following procedures given in EPA Method 25A.

Method 25A is an instrument based method in which the stack gas is introduced directly to a flame ionization detector (FID) without first separating the components. In Method 25A,

sampling is accomplished by extracting a gas stream from the stack effluent and transferring it via heated non-reactive tubing to the FID analyzer under very controlled temperature and pressure conditions. The FID measures the quantity of carbon containing molecules, and is calibrated by a gas standard, which in this case is the three carbon alkane, propane (C_3H_8) . The FID will give a response relative to the calibration standard and results are expressed in terms of the gas used for calibration. Because the FID responds to all carbon containing compounds, methane (CH_4) and other exempt compounds are included in the total hydrocarbon results.

Mass emission rates for all analytes were calculated using laboratory analytical results, measured source data and appropriate process data.

The specific steps used in this sampling program are summarized below.

2.2.1. Individual Sampling Events

Test HRa was designed to evaluate emissions from the production of molds using the RCT digital printing system. This was accomplished by setting up the TGOC analyzer and two VOSTs on the machine vent. Air flows across the top of the print box and is drawn from the machine at the rear where it is vented through a 4" duct out of the room. The flow rate of the air through the duct was nominally 16 scfm. Because the print box is enclosed on three sides, air flows only over the sand layer being printed. Any emissions generated from the curing of the binder on previously printed layers must diffuse vertically through the sand bed to exit the box.

Two sample probes were located on the vertical section of the duct above the printing machine at a location determined through the procedures outlined in EPA Method 1, one probe for each VOST. The TGOC analyzer was connected to one channel of one VOST. The emission monitoring and collection equipment and location are shown in Figure 2-6 from both the front and side view.



The emissions generated during the operation of the digital printer were transported through the sample probes and sampling lines into the VOSTs.

Air samples were collected during the build of one complete print box in six dissimilar runs, ranging from a 1 hour "storage" period where no active printing was taking place, to the over 35 hour period which was required to print the four complete 4-on gear molds for a full job box. Figure 2-7 shows the schematic layout of the print box and time and event details for individual runs. Two VOSTs were needed to accommodate the complicated sampling scheme, as more channels were needed to collect samples during overlapping run times than one VOST could provide. Even with the two VOSTs, however, there were not enough available channels on the two trains to provide samples for replicate runs needed for statistical analysis.

TECHNIKON # 1412-124 HRA

JANUARY 2008



2.2.2. Test Plan Review and Approval

The proposed test plan was reviewed and approved by the Technikon staff and by CERP Working Group Chairs as appropriate.

2.2.3. Data Reduction, Tabulation and Preliminary Report Preparation

Data calculations for determining emission concentrations resulting from the specific test plan outlined in Appendix A were based on process and emission parameters. The analytical results of the emissions sampling provided the mass of each analyte in the sample. The total mass of the analyte emitted was calculated by multiplying the mass of analyte in the sample by the ratio of total stack gas volume to sample volume. The total stack gas volume was calculated from the measured stack gas velocity and duct diameter and corrected to dry standard conditions using the measured stack pressures, temperatures, gas molecular weight, and moisture content.

Usually, the total mass of analyte is then divided by the weight of the sand or weight of binder to provide emissions data in pounds of analyte per ton of sand, or pounds of analyte per pound of binder. However, due to the complex nature of the digital printing process emissions calculated on a lb per lb binder or lb per ton sand basis were not representative or reproducible.

Because there was no common binder or sand basis for calculations for the disparate runs, the method of normalization of emissions had to be altered. Each layer printed, although somewhat symmetrical in the pattern in all directions, were not identical from an emissions point of view, especially in the x-z direction. The amount of binder deposited was dependent on what slice of the mold was being printed. Layers – and therefore probably emissions – were cumulative. In addition, for the storage test, no binder or sand was being deposited. Emissions are therefore reported as lbs per event and lbs per printing time and are given in Section 3.

2.2.4. Report Preparation and Review

The preliminary draft report was created and reviewed by Process Team and Emissions Team members to ensure its completeness, consistency with the test plan, and adherence to QA/QC procedures. Appropriate observations, conclusions, and recommendations were added to the report to produce a draft report. The draft report was then reviewed by senior management and comments were incorporated into a draft final report prior to final signature approval and distribution.

2.3. Quality Assurance and Quality Control (QA/QC) Procedures

Detailed QA/QC and data validation procedures for the process parameters, stack measurements, and laboratory analytical procedures were included in the "Technikon

Emissions Testing and Analytical Testing Standard Operating Procedures" publication. In order to ensure the timely review of critical quality control parameters, the following procedures were followed:

- Specific process parameters for this test were under constant surveillance by process engineers to ensure that the machine was operating properly and that all printing and mold parameters were maintained within the prescribed control ranges.
- The source (stack) and sampling parameters, analytical results and corresponding laboratory QA/QC data were reviewed by the Emissions Measurement Team to confirm the validity of the data. Senior management of Analytical Measurement Technologies reviewed recommendations regarding individual sample data that should be invalidated. Invalidated data were not used in subsequent calculations.

3.0 TEST RESULTS

Air samples were collected during the build of one complete print box in six dissimilar runs, ranging from a 1 hour "storage" period where no active printing or sand deposition was taking place, to the over 35 hour time period which was required for a completed print box for four 4-on gear copes and drags. The printing of a second print box of the same layout was planned to provide duplicates for all six samples taken during the first print box, but the machine failed several hours into the printing and could not be restarted. Duplicate runs could not be obtained on a single print box due to the length of required sampling time and the limitation of the number of available VOST channels. Duplicate samples and other quality control samples were taken for each analysis type to ensure accuracy of analysis.

Results presented in the tables of this report have been background corrected. When sample measurements are made, the observed result includes the contribution of the analyte in the sample, plus a response due to the background contribution found from the blank. The net analyte sample concentration is therefore the amount of the analyte, if any, found in the blank subtracted from the amount of analyte found in the sample. Background correcting the data allows determination of the emissions resulting only from the specific materials tested, and not those that may be present in the ambient air of the research foundry during the testing period.

Chemical compounds which were chosen for sampling and analysis are based on chemical and operational parameters, and are termed "target analytes" (TA). Speciated sampling was conducted for formaldehyde, furfural, furfuryl alcohol, and sulfur dioxide. Samples were also taken using charcoal tubes for general gas chromatography-mass spectrometry (GC/MS) analysis. Average results for the relative airborne emissions for the single print box are presented in Table 3-1 as lbs of emissions produced per sampling event. Sample names are given separate letter designations, and are given in Table 3-1.

	Me	Measured Mold Making and Storage Sampling Event						
	1 Mold Make 2 Mold Make 3 Mold Make 2 Mold Make 3 M			2 Mold Make 3 Storage	1 Storage	4 Mold Make 4 Storage		
Sample Name	HRa001	HRa002	HRa003	HRa004	HRa005	HRa006		
Letter Designation	0	D	0	D	E	-		
Letter Designation	A	В	C	D	E	F		
Isopropyl Alcohol	A 2.12E-05	5.20E-03	1.03E-04	3.42E-05	<u>Е</u> 1.04Е-06	+ 4.20E-05		
Isopropyl Alcohol Furfuryl Alcohol	A 2.12E-05 3.81E-02	5.20E-03 7.91E-02	1.03E-04 1.19E-01	D 3.42E-05 7.64E-02	<u>Е</u> 1.04Е-06 7.61Е-04	+ 4.20E-05 1.55E-01		
Isopropyl Alcohol Furfuryl Alcohol Furfuryl Alcohol Furfural	A 2.12E-05 3.81E-02 ND	5.20E-03 7.91E-02 ND	1.03E-04 1.19E-01 ND	D 3.42E-05 7.64E-02 ND	E 1.04E-06 7.61E-04 ND	+ 4.20E-05 1.55E-01 1.87E-04		
Isopropyl Alcohol Furfuryl Alcohol Furfuryl Alcohol Furfural Sulfur Dioxide	A 2.12E-05 3.81E-02 ND 5.21E-05	5.20E-03 7.91E-02 ND 1.11E-04	1.03E-04 1.19E-01 ND 1.72E-04	D 3.42E-05 7.64E-02 ND 1.15E-04	E 1.04E-06 7.61E-04 ND ND	+ 4.20E-05 1.55E-01 1.87E-04 2.39E-04		
Isopropyl Alcohol Furfuryl Alcohol Furfuryl Alcohol Furfural Sulfur Dioxide Formaldehyde	A 2.12E-05 3.81E-02 ND 5.21E-05 1.28E-04	5.20E-03 7.91E-02 ND 1.11E-04 2.16E-04	1.03E-04 1.19E-01 ND 1.72E-04 5.64E-04	3.42E-05 7.64E-02 ND 1.15E-04 2.07E-04	E 1.04E-06 7.61E-04 ND ND 2.05E-05	4.20E-05 1.55E-01 1.87E-04 2.39E-04 3.88E-04		

Table 3-1	Test HRa Emissions Results – Ib per Sampling Event
-----------	--

I=Invalidated data ND=Non-Detect

The six runs sampled under Test HRa were intentionally scheduled in such as way that a determination of emissions from any multiple of desired mold and storage emission events could be calculated from the results measured under this test. In other words, it was thought that emissions from the single mold making event sampled in Run HRa001 (given a sample designation "A") added to the emissions from the single storage event sampled in Run HRa005 (given a sample designation "E"), could accurately represent a single combined mold make/storage event. Although this combination wasn't actually measured, it theoretically could be calculated from these individual single measured events, and should also be equal to one quarter of the measured emissions from the 4 mold make/4 storage event sampled under Run HRa006 (given a sample designation "F"). Several multiples of the single digital mold making event from Run "A" and the single mold storage event from Run "E" were calculated and then compared to measured multiple make and storage events.

Various mathematical combinations of events "A" through "F" were calculated to correspond with measured events (also given letter designations). To determine how closely emissions from the calculated events compared to measured emissions, Equation 1 was used to determine the percent difference between the measured and calculated events. The percent difference results are given in Table 3-2. The mathematical combinations and their letter designations are also given in Table 3-2.

Equation 1

$$\% Diff = \frac{|x_1 - x_2|}{\left(\frac{x_1 + x_2}{2}\right)} \times 100$$

Table 3-2Percent Difference Between Calculated and Measured Multiple
Mold and Storage Events

	Mold Making and Storage Sampling Event						
	2 Mold Make 3		2 Mold Make 3 Mold Make 2		4 Mold Make		
Comparison Designations	BB [#] & B	BB [#] & B BB' & B		DD & D FF & F		FF' & F	
Isopropyl Alcohol	197	199	44	28	143	197	
Furfuryl Alcohol	1	0	3	3	133	0	
Furfural	NA	200	NA	NA	120	200	
Sulfur Dioxide	7	11	10	10	132	5	
Formaldehyde	38	18	28	42	137	9	
[#] Where	BB=2A+2E	BB'=F-D	CC=3A+2E	DD=2A+3E	FF=4A+4E	FF'=B+D	

Each layer printed, although somewhat symmetrical in the physical pattern in all directions, was not identical from an emissions point of view, especially along the vertical axis. The amount of binder deposited was dependent on what slice of the mold was being printed. Also, as slices built up, the sand layers, as well as the binder amount and air emissions, accumulated.

Digital printing does not have continuous or consistent binder usage, nor is the binder deposition uniform throughout the print box. And, for this digital printing test, there was no common consistent binder or sand basis for calculating emissions for all of the disparate runs. These limitations preclude the normalization of emissions and determination of emission factors on the customary lb/lb binder or lb/lb sand basis. Initial attempts to normalize by layers of sand deposited during construction of each sampling event were also unsuccessful and couldn't be used for measuring emissions from the mold storage event, HRA005 (designation "E"), as the machine was idle and no sand layers were deposited during this sampling event. To accommodate all the variations on sampling events, emissions were calculated both as lbs per sampling event and lbs per printing time. The only reproducible emission factors that could be determined were calculated

by normalizing emissions by printing time on an hourly basis, with individual event and average results shown in Table 3-3.

Measured Sampling Event	1 Mold Make	2 Mold Make 1 Storage	3 Mold Make 2 Storage	2 Mold Make 3 Storage	1 Storage	4 Mold Make 4 Storage	Average, Ib/hr
Sample Name	HRa001	HRa002	HRa003	HRa004	HRa005	HRa006	
Isopropyl alcohol	2.55E-06	3.09E-04	4.01E-06	2.01E-06	1.04E-06	1.19E-06	NA
Furfuryl Alcohol	4.56E-03	4.70E-03	4.65E-03	4.49E-03	7.62E-04	4.40E-03	3.93E-03
Furfural	ND	ND	ND	ND	ND	5.29E-06	5.29E-06
Sulfur Dioxide	6.24E-06	6.62E-06	6.71E-06	6.73E-06	ND	6.76E-06	6.61E-06
Formaldehyde	1.54E-05	1.28E-05	2.20E-05	1.22E-05	2.05E-05	1.10E-05	1.56E-05
[#] GCMS	8.27E-06	ND	4.24E-06	7.01E-06	1.96E-05	3.47E-06	8.52E-06

Tabla 2.2	Tast UDa Emissians Dasults	Ih	nor hour	of di	aital	nrinting	+ tima
able s-s	ΤΕΣΙ ΠΚΑ ΕΠΙΣΣΙΟΠΣ ΚΕΣΔΙΙΣ -	- 10	pernour	u u	yılar	printing	lume

NA=Not Applicable

ND= Non Detect

[#] Adjusted total emissions represented by sum of all components found in GCMS profile relarive to pentafluorobenzene.

Included in Table 3-3 are average results for each species, including numbers for all compounds found in the GCMS analysis. The GCMS numbers are included for reference purposes only. These numbers are not quantitative, having been calculated relative to the internal standard pentaflurobenzene since few calibration standards were run. Additionally, no average isopropyl alcohol number is given, as the amount used for cleaning the print head is highly variable.

3.1. Discussion of Results

The individual chemical compounds targeted for collection and analyses from airborne emissions for this test were chosen based on the chemistry of the binder and activator used as well as analytes historically targeted.

The lb/sampling event results given in Table 3-1 are shown as bar charts for total GC/MS and speciated data in Figure 3-1. As a note, the sample number on the x-axis of the figure is in the order of expected amount of emissions. That is, from the least expected amount of emissions (the one hour storage sampled under Run HRa005), to the most expected emissions (total build box – four mold makes and four storage events sampled under Run HRa006), a clear increasing trend is visible as the number of mold making and storage

events increases for those analytes directly related to the binder chemistry. This includes everything but the isopropyl alcohol, which is the cleaning solvent for the print head. Furfural is not present in the binder, but can be formed from oxidation of furfuryl alcohol.

The generation and measurement of emissions from the digital printing process was much more complex than anticipated. Numerous physical processes are associated with the deposition of liquid binder on a single sand layer, which are then built up layer upon layer to complete a three dimensional object before the binder cures on a single layer. One complication to measuring emissions from this technology relates to complex diffusion process. Any emissions generated from the curing of the binder on primary printed layers must diffuse vertically through the bed. As the bed is being built up layer by layer, emissions are also increasing since the total amount of binder deposited accumulates with increasing layers. The diffusional properties through the bed are simultaneously changing as the mass of sand increases with each layer, compressing the lower sand layers and changing diffusion paths.

Reproducible emission factors were determined by normalizing sand, binder, and machine variation. This was accomplished through calculating emissions in lbs per printing time on an hourly basis. Emissions calculated on a lb/hour of printing time basis given in Table 3-3 are shown in Figure 3-2. Similar to Figure 3-1, sample number is in the order of the least expected amount of emissions to the most. Considering the complicated emissions situation from digital printing, results within an analyte group differ by only a few percent, especially when excluding the one hour storage sample from HRa005. This is most noticeable for those analytes directly related to the binder chemistry, which includes sulfur dioxide, furfuryl alcohol and formaldehyde.

JANUARY 2008



Figure 3-1 Order of Anticipated Increase in Emissions with Number of Mold and Storage Events, Ibs per event



Figure 3-2 Mass Emission Rate, Ib/hour of printing

Because of the large percent differences between some of the measured and calculated events, as seen from Table 3-2, it is evident that emissions were not entirely additive. For example, in comparing the full print box emissions (calculated "FF" to measured "F"), cumulative and generated emissions that were not sampled in the short one hour storage sampling time used to calculate "FF" must have been sampled during the long 35 hour sampling period of "F" resulting in differences over 100%. For all the other, shorter, event combinations the emissions between the measured and calculated events are close, especially for the analytes directly related to the binder chemistry.

A comprehensive review of the GC/MS analysis revealed a complex mixture for emissions. It had been anticipated that since the disclosed binder composition contained relatively few components, and that emissions would be mainly evaporative, the GC/MS profiles would show few and small peaks. This was clearly not the case, as can be seen in Figure 3-3 using Run HRa003 as an example. The main peaks identified consisted of many furan-based derivatives. Compounds traditionally targeted using charcoal tubes, if present, were in extremely minor amounts except for toluene.





Confirmatory GC/MS analysis showed an average of over 230 peaks in the chromatogram, although over 100 peaks accounted for the majority of the mass, as determined by peak area. The species contributing the largest percent to emissions for every run was furfuryl alcohol. Listings of several of the main components identified in the GCMS chromatogram are given in alphabetical order in Table 3-4.

The four appendices in this report contain detailed information regarding testing, sampling, data collection and results for each sampling event. Appendix A contains test plans, instructions, and the sampling plans for Test HRa. Appendix B contains details of the digital printing operation. Appendix C contains continuous monitor charts. The charts are presented to show TGOC, time-dependent emissions profiles for each individual emissions run. These charts have not been background corrected. Appendix D contains acronyms and abbreviations.

Table 3-4Major Compounds from GC/MSAnalysis

1 3-Isobutyl-4,5-dimethyl-3H-isobenzo 71073 1000187-23-3 50
1H-Inden-1-one, 2,3-dihydro-
1H-Pyrrole, 1-(2-furanylmethyl)-
1-Pentanol
2-Furancarboxaldehyde
2-Furancarboxaldehyde, 5-(2-fu
2-Furancarboxaldehyde, 5-(2-furanylmethyl)-
2-Furanmethanol
2H-1-Benzopyran-2-one 3,4-dimethyl-
2H-1-Benzopyran-2-one 3,4-dimethyl-
2-Pentanone
Acetic acid, butyl ester
Benzene, 1,2,3,5-tetramethyl-
Benzofuran, 2-methyl-
Benzyl Alcohol
Bicyclo[6.3.0.0(1,8)]undeca-1(8),9-diene, 11,11-dimethyl-
Ethanone, 1,1'-(1,4-phenylene)bis-
Ethanone, 1,1'-(1,4-phenylene)bis-
Ethanone, 1-oxiranyl
Furan, 2-(2-furanylmethyl)-5-methy
Furan, 2-(2-furanylmethyl)-5-methy
Furan, 2,2'-(1,2-ethenediyl)bi
Furan, 2,2'-[oxybis(methylene)
Furan, 2,2'-methylenebis-
Furan, 2,2'-methylenebis[5-met
Furan, 2,3-dihydro-4-methyl-
Furan, 2,5-bis(2-furanylmethyl
Furan, 2,5-dimethyl-
Furan, 2-methyl-
Furan, 3-methyl-
Furfural
Naphthalene, 1-ethyl-1,2,3,4-tetrah
Octane
Phenol, 2-ethoxy-5-[1-propenyl]-
Phenol, 4-butyl-
Propanoic acid, 2-methyl-, 2-ethyl
Pyroxyfur
Tetradecane
Toluene
unknown at r.t. 55.779
unknown at r.t. 63.25
unknown at r.t. 63.25

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APPENDIX A TEST AND SAMPLE PLANS AND PROCESS INSTRUCTIONS

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Technikon Test Plan

page 1 of 3

Fill-in and check all that apply							
CONTRACT NUMBER	: 1412 Task Number 124 Double Alpha HR-A						
• Site:	On Site at Research Foundry D Off Site at						
• DATE RANGE:	From <u>Jun. 1, 07</u> to <u>Jul. 30, 07</u>						
• TEST OBJECTIVE:	Emissions Testing Mechanical Properties Casting Quality Comparison to						
• PROCESSES:	Pouring Cooling Shakeout Mixing Making Storage Other						
◆ TEST TYPE:	Baseline Product Other						
◆ Metal:	Iron Aluminum Steel Other Alloy Pour Temp: F						
◆ Runs:	Number for Conditioning Duration minutes Number for Testing Samples <u>6 samples per box, total of 12</u> Duration <u>Variable</u> . Dependant on time to make 1-4 <u>molds</u> , minutes						
• PROPERTIES TO BE TESTED:	Mold Strength Moisture Content X 1800 °F LOI% C °F Volatiles						
• RESULTS TO BE ANALYZED AND REPORTED:	Image: Sign Sign Sign Sign Sign Sign Sign Sign						
• Brief Overview:	This part of the test will measure emissions from the making and storage of 8 printed irregular gear molds. The molds will be printed in 2 boxes (4 per box.) There will be an additional mold added from a run that was used to estimate a measurement range for the THC.						
• Additional Comments:	The molds will be wrapped in plastic after being mated out of the print box. The sampling train will continue to run for one (1) hour after the ExOne machine has quite printing.						

JANUARY 2008

Technikon Test Plan page 2 of 3					
Fill-in and check all that apply					
CONTRACT NUMBER: 1412 TASK NUMBER 124 DOUBLE ALPHA HR-A					
	Cores	Molds	Other		
◆ Pattern:	Step	Step Star Star Star Other	Dogbone Shakeout Flowability Other		
	Number	Number <u>8</u>	Number		
	Number Cavities	Number Cavities 4	Number Cavities		
	Storage Temp:°F Storage Age: Dimensions:	Storage Temp: <u>70-90</u> °F Storage Age: <u>>40 hours</u> Dimensions:	Storage Temp:°F Storage Age: Dimensions:		
	Standard (24x24x10/10) Other	Standard (24x24x10/10) Other	Standard (24x24x10/10) Other		
• Binder :	Cold boxWarm boxHot boxNo-bakeShellOilOtherConcentrationKatio ($\frac{P1}{P2}$)Product Name(s)	Cold boxWarm boxHot boxNo-bakeShellOilOther PrintedConcentration 1.5% (BOS)Ratio $(\frac{P1}{P2})$ Product Name(s) Prometal RCTBinder FB-001 EU	Cold boxWarm boxHot boxNo-bakeShellOilOtherConcentrationConcentration(BOS)Ratio ($\frac{P1}{P2}$)Product Name(s)		
Chemistry:	 Phenolic Urethane Furan Low Emission (inc. Sodium Silicate) Epoxy-Acrylic Alkaline Phenolic Ester Other 	 Phenolic Urethane Furan Low Emission (inc. Sodium Silicate) Epoxy-Acrylic Alkaline Phenolic Ester Other 	 Phenolic Urethane Furan Low Emission (inc. Sodium Silicate) Epoxy-Acrylic Alkaline Phenolic Ester Other 		
 CATALYST: 	CO ₂ Cured SO ₂ Cured Acid Cured TEA Cured Hot Air Cured Methyl Formate Cured Concentration BOS Concentration BOR	CO ₂ Cured SO ₂ Cured CO ₂ Cured SO ₂ Cured Cured TEA Cured Hot Air Cured Methyl Formate Cured Concentration 0.32% BOS ConcentrationBOR Other Prometal RCT Activator EC001-EU (sufformic acid)	CO2 Cured SO2 Cured CO2 Cured SO2 Cured Cured SO2 Cured Hot Air Cured Methyl Formate Cured Concentration BOS Concentration BOR Other		

Techn	ikon Test Plan		page 3 of 3
	Fill-in	and check all that apply	
• Contract Numb	ег: 1412 Тазк Numb	er 124 Double Alpha	HR-A
	Cores	Molds	Other
• SAND:	Greensand No-Bake Conternation Other Additives to yield %LOI Product Name(s)	Greensand No-Bake Greensand No-Bake Greensand No-Bake Greensand Additives Koyiel No-Bake Koyiel Koyi	Greensand No-Bake Conternation Other Additives to yield %LOI Product Name(s)
• Release Agent:	Concentration Application Method Product Name(s)	Concentration Application Method Product Name(s)	Concentration Application Method Product Name(s)
◆ Coating:	None All Runs Conditioning Runs Only Test Runs Only Baumé Other Application Method Drying Method Product Name(s)	None All Runs Conditioning Runs Only Test Runs Only Baumé Other Application Method Drying Method Product Name(s)	

This test plan routed to or reviewed by:

- Senior Process Engineer
- Technical Director/Foundry ManagerDirector of Measurement Technologies
- Vice President of Operations •
- Applicable Steering Committee Members •

JANUARY 2008

	(1)	-									
BOX ONE Method	Sample #	Data	Sample	Duplicate	Blank	Breakthrough	Spike	Spike Duplicate	Flow (ml/min)	Train Channel	Comments: <u>Run 6</u> is the comprehensive 40 hour run starting at the beginning of mold 1 (all molds) and will end at one hour (storage) after the completion of mold 4, while <u>Run 3</u> will start at the beginning of mold 1 and run until the completion of mold 3
THC Train	HR003/ HR006										
TO (710	HRUU3										
10-17 MS	HR00301		1						60	1	Carbopak charcoal
10-17 MS	HR00310				1						Carbopak charcoal
NIOSH 2505	HR00302		1						60	2	Porapak Q (SKC 226-115)
NIOSH 2505	HR00303				1				0		Porapak Q (SKC 226-115)
NIOSH 2529	HR00304		1						60	3	XAD-2 (SKC 226-117)
NIOSH 2529	HR00305				1				0		XAD-2 (SKC 226-117)
OSHA ID200	HR00306		1						100	4	100/50 mg Carbon Bead (SKC 226-80)
OSHA ID200	HR00307				1				0		100/50 mg Carbon Bead (SKC 226-80)
TO11	HR00308		1						100	5	DNPH Silica Gel (SKC 226-119)
TO11	HR00309				1				0		DNPH Silica Gel (SKC 226-119)
	Moisture		1						100	6	TOTAL
тнс	HR006	x									TOTAL
TO-17 MS	HR00601		1						60	7	Carbopak charcoal
TO-17 MS	HR00606					1			60	7	Carbopak charcoal
NIOSH 2505	HR00602		1						60	8	Porapak Q (SKC 226-115)
NIOSH 2529	HR00603		1						60	9	XAD-2 (SKC 226-117)
OSHA ID200	HR00604		1						100	10	100/50 mg Carbon Bead (SKC 226-80)
TO11	HR00605		1						100	11	DNPH Silica Gel (SKC 226-119)
	Moisture		1						100	12	TOTAL
	Excess								2000	13	Excess

RESEARCH FOUNDRY HR(a) - SERIES SAMPLE PLAN

BOX ONE Method	Sample #	Data	Sample	Duplicate	Blank	Breakthrough	Spike	Spike Duplicate	Flow (ml/min)	Train Channel	Comments: Run 1 begins at the beginning of the first mold and ends when the first mold is completed, while run 2 begins at the beginning of the first mold and ends when the second mold is completed
Non-THC Train	HR001/										
	HR002										
TO-17 MS	HR00201		1						100	1	Carbopak charcoal
NIOSH 2505	HR00202		1						100	2	Porapak Q (SKC 226-115)
NIOSH 2529	HR00203		1						100	3	XAD-2 (SKC 226-117)
OSHA ID200	HR00204		1						200	4	100/50 mg Carbon Bead (SKC 226-80)
TO11	HR00205		1						200	5	DNPH Silica Gel (SKC 226-119)
	Moisture		1						200	6	TOTAL
TO-17 MS	HR00101		1						100	7	Carbopak charcoal
NIOSH 2505	HR00102		1						100	8	Porapak Q (SKC 226-115)
NIOSH 2529	HR00103		1						100	9	XAD-2 (SKC 226-117)
OSHA ID200	HR00104		1						200	10	100/50 mg Carbon Bead (SKC 226-80)
TO11	HR00105		1						200	11	DNPH Silica Gel (SKC 226-119)
	Moisture		1						200	12	TOTAL
	Excess								2000	13	Excess

RESEARCH FOUNDRY HR(a) - SERIES SAMPLE PLAN

BOX ONE Method	Sample #	Data	Sample	Duplicate	Blank	Breakthrough	Spike	Spike Duplicate	Flow (ml/min)	Train Channel	Comments: Run 4 begins when the 3rd mold is started and continues until the fourth mold has been completed. The remaining channels on the train shall be an exact replicate, beginning and ending at the same time.
Non-THC Train	HR004										
TO-17 MS	HR00401		1						100	1	Carbopak charcoal
NIOSH 2505	HR00402		1						100	2	Porapak Q (SKC 226-115)
NIOSH 2529	HR00403		1						100	3	XAD-2 (SKC 226-117)
OSHA ID200	HR00404		1						200	4	100/50 mg Carbon Bead (SKC 226-80)
TO11	HR00405		1						200	5	DNPH Silica Gel (SKC 226-119)
	Excess								200	6	BLOCKED
TO-17 MS	HR00406			1					100	7	Carbopak charcoal
NIOSH 2505	HR00407			1					100	8	Porapak Q (SKC 226-115)
NIOSH 2529	HR00408			1					100	9	XAD-2 (SKC 226-117)
OSHA ID200	HR00409			1					200	10	100/50 mg Carbon Bead (SKC 226-80)
TO11	HR00410			1					200	11	DNPH Silica Gel (SKC 226-119)
	Moisture		1						200	12	TOTAL
	Excess								2000	13	Excess

BOX ONE Method	Sample #	Data	Sample	Duplicate	Blank	Breakthrough	Spike	Spike Duplicate	Flow (ml/min)	Train Channel	Comments: One hour storage period at completion of fourth box
THC Train	HR005										
TO-17 MS	HR00501		1						500	1	Carbopak charcoal
NIOSH 2505	HR00502		1						500	2	Porapak Q (SKC 226-115)
NIOSH 2529	HR00503		1						500	3	XAD-2 (SKC 226-117)
OSHA ID200	HR00504		1						500	4	100/50 mg Carbon Bead (SKC 226-80)
TO11	HR00505		1						500	5	DNPH Silica Gel (SKC 226-119)
	Moisture		1						500	6	TOTAL
	Excess								100	7	BLOCKED
	Excess								100	8	BLOCKED
	Excess								200	9	BLOCKED
	Excess								200	10	BLOCKED
	Excess								200	11	BLOCKED
	Excess								200	12	BLOCKED
	Excess								2000	13	Excess

JANUARY 2008

BOX TWO Method	Sample #	Data	Sample	Duplicate	Blank	Breakthrough	Spike	Spike Duplicate	Flow (ml/min)	Train Channel	Comments: <u>Run 12</u> is the comprehensive 40 hour run starting at the beginning of mold 1 (all molds) and will end at one hour (storage) after the completion of mold 4, while <u>Run 9</u> will start at the beginning of mold 1 and run until the completion of mold 3
THC Train	HR009/HR012										
	HR009										
TO-17 MS	HR00901		1						60	1	Carbopak charcoal
NIOSH 2505	HR00902		1						60	2	Porapak Q (SKC 226-115)
NIOSH 2529	HR00903		1						60	3	XAD-2 (SKC 226-117)
OSHA ID200	HR00904		1						100	4	100/50 mg Carbon Bead (SKC 226-80)
TO11	HR00905		1						100	5	DNPH Silica Gel (SKC 226-119)
	Moisture		1						100	6	TOTAL
тнс	HR012	x									TOTAL
TO-17 MS	HR01201		1						60	7	Carbopak charcoal
NIOSH 2505	HR01202		1						60	8	Porapak Q (SKC 226-115)
NIOSH 2529	HR01203		1						60	9	XAD-2 (SKC 226-117)
OSHA ID200	HR01204		1						100	10	100/50 mg Carbon Bead (SKC 226-80)
TO11	HR01205		1						100	11	DNPH Silica Gel (SKC 226-119)
	Moisture		1						100	12	TOTAL
	Excess								2000	13	Excess

RESEARCH FOUNDRY HR(a) - SERIES SAMPLE PLAN

BOX TWO Method	Sample #	Data	Sample	Duplicate	Blank	Breakthrough	Spike	Spike Duplicate	Flow (ml/min)	Train Channel	Comments: Run 7 begins at the beginning of the first mold and ends when the first mold is completed, while run 8 begins at the beginning of the first mold and ends when the second mold is completed
Non-THC Train	HR007/										
	HR008										
TO-17 MS	HR00801		1						100	1	Carbopak charcoal
NIOSH 2505	HR00802		1						100	2	Porapak Q (SKC 226-115)
NIOSH 2529	HR00803		1						100	3	XAD-2 (SKC 226-117)
OSHA ID200	HR00804		1						200	4	100/50 mg Carbon Bead (SKC 226-80)
TO11	HR00805		1						200	5	DNPH Silica Gel (SKC 226-119)
	Moisture		1						200	6	TOTAL
TO-17 MS	HR00701		1						100	7	Carbopak charcoal
NIOSH 2505	HR00702		1						100	8	Porapak Q (SKC 226-115)
NIOSH 2529	HR00703		1						100	9	XAD-2 (SKC 226-117)
OSHA ID200	HR00704		1						200	10	100/50 mg Carbon Bead (SKC 226-80)
TO11	HR00705		1						200	11	DNPH Silica Gel (SKC 226-119)
	Moisture		1						200	12	TOTAL
	Excess								2000	13	Excess

RESEARCH FOUNDRY HR(a) - SERIES SAMPLE PLAN

BOX TWO Method	Sample #	Data	Sample	Duplicate	Blank	Breakthrough	Spike	Spike Duplicate	Flow (ml/min)	Train Channel	Comments: Run 10 begins when the 3rd mold is started and continues until the fourth mold has been completed.
Non-THC Train	HR010										
	Excess								100	1	BLOCKED
	Excess								100	2	BLOCKED
	Excess								100	3	BLOCKED
	Excess								200	4	BLOCKED
	Excess								200	5	BLOCKED
	Excess								200	6	BLOCKED
TO-17 MS	HR01001		1						100	7	Carbopak charcoal
NIOSH 2505	HR01002		1						100	8	Porapak Q (SKC 226-115)
NIOSH 2529	HR01003		1						100	9	XAD-2 (SKC 226-117)
OSHA ID200	HR01004		1						200	10	100/50 mg Carbon Bead (SKC 226-80)
TO11	HR01005		1						200	11	DNPH Silica Gel (SKC 226-119)
	Moisture		1						200	12	TOTAL
	Excess								2000	13	Excess

BOX TWO Method	Sample #	Data	Sample	Duplicate	Blank	Breakthrough	Spike	Spike Duplicate	Flow (ml/min)	Train Channel	Comments: One hour storage period at completion of fourth box
THC Train	HR011										
TO-17 MS	HR01101		1						500	1	Carbopak charcoal
NIOSH 2505	HR01102		1						500	2	Porapak Q (SKC 226-115)
NIOSH 2529	HR01103		1						500	3	XAD-2 (SKC 226-117)
OSHA ID200	HR01104		1						500	4	100/50 mg Carbon Bead (SKC 226-80)
TO11	HR01105		1						500	5	DNPH Silica Gel (SKC 226-119)
	Moisture		1						500	6	TOTAL
	Excess								100	7	BLOCKED
	Excess								100	8	BLOCKED
	Excess								200	9	BLOCKED
	Excess								200	10	BLOCKED
	Excess								200	11	BLOCKED
	Excess								200	12	BLOCKED
	Excess								2000	13	Excess

JANUARY 2008

RESEARCH FOUNDRY HR(a) - SERIES SAMPLE PLAN

BOX THREE Method	Sample #	Data	Sample	Duplicate	Blank	Breakthrough	Spike	Spike Duplicate	Flow (ml/min)	Train Channel	Comments: <u>Run 12a</u> is the comprehensive 40 hour run starting at the beginning of mold 1 (all molds) and will end at one hour (storage) after the completion of mold 4, while <u>Run 9a</u> will start at the beginning of mold 1 and run until the completion of mold 3
THC Train	HR009a/HR012a										
	HR009a										
TO-17 MS	HR00901a		1						60	1	Carbopak charcoal
NIOSH 2505	HR00902a		1						60	2	Porapak Q (SKC 226-115)
NIOSH 2529	HR00903a		1						60	3	XAD-2 (SKC 226-117)
OSHA ID200	HR00904a		1						100	4	100/50 mg Carbon Bead (SKC 226-80)
TO11	HR00905a		1						100	5	DNPH Silica Gel (SKC 226-119)
	Moisture		1						100	6	TOTAL
THC	HR012	X									TOTAL
TO-17 MS	HR01201a		1						60	7	Carbopak charcoal
NIOSH 2505	HR01202a		1						60	8	Porapak Q (SKC 226-115)
NIOSH 2529	HR01203a		1						60	9	XAD-2 (SKC 226-117)
OSHA ID200	HR01204a		1						100	10	100/50 mg Carbon Bead (SKC 226-80)
TO11	HR01205a		1						100	11	DNPH Silica Gel (SKC 226-119)
	Moisture		1						100	12	TOTAL
	Excess								2000	13	Excess

BOX THREE Method	Sample #	Data	Sample	Duplicate	Blank	Breakthrough	Spike	Spike Duplicate	Flow (ml/min)	Train Channel	Comments: Run 7a begins at the beginning of the first mold and ends when the first mold is completed, while run 8a begins at the beginning of the first mold and ends when the second mold is completed
Non-THC Train	HR007a/										
	HR008a										
TO-17 MS	HR00801a		1						100	1	Carbopak charcoal
NIOSH 2505	HR00802a		1						100	2	Porapak Q (SKC 226-115)
NIOSH 2529	HR00803a		1						100	3	XAD-2 (SKC 226-117)
OSHA ID200	HR00804a		1						200	4	100/50 mg Carbon Bead (SKC 226-80)
TO11	HR00805a		1						200	5	DNPH Silica Gel (SKC 226-119)
	Moisture		1						200	6	TOTAL
TO-17 MS	HR00701a		1						100	7	Carbopak charcoal
NIOSH 2505	HR00702a		1						100	8	Porapak Q (SKC 226-115)
NIOSH 2529	HR00703a		1						100	9	XAD-2 (SKC 226-117)
OSHA ID200	HR00704a		1						200	10	100/50 mg Carbon Bead (SKC 226-80)
TO11	HR00705a		1						200	11	DNPH Silica Gel (SKC 226-119)
	Moisture		1						200	12	TOTAL
	Excess								2000	13	Excess

RESEARCH FOUNDRY HR(a) - SERIES SAMPLE PLAN

BOX THREE Method	Sample #	Data	Sample	Duplicate	Blank	Breakthrough	Spike	Spike Duplicate	Flow (ml/min)	Train Channel	Comments: Run 10 begins when the 3rd mold is started and continues until the fourth mold has been completed.
Non-THC Train	HR010										
	Excess								100	1	BLOCKED
	Excess								100	2	BLOCKED
	Excess								100	3	BLOCKED
	Excess								200	4	BLOCKED
	Excess								200	5	BLOCKED
	Excess								200	6	BLOCKED
TO-17 MS	HR01001		1						100	7	Carbopak charcoal
NIOSH 2505	HR01002		1						100	8	Porapak Q (SKC 226-115)
NIOSH 2529	HR01003		1						100	9	XAD-2 (SKC 226-117)
OSHA ID200	HR01004		1						200	10	100/50 mg Carbon Bead (SKC 226-80)
TO11	HR01005		1						200	11	DNPH Silica Gel (SKC 226-119)
	Moisture		1						200	12	TOTAL
	Excess								2000	13	Excess

BOX THREE Method	Sample #	Data	Sample	Duplicate	Blank	Breakthrough	Spike	Spike Duplicate	Flow (ml/min)	Train Channel	Comments: One hour storage period at completion of fourth box
THC Train	HR011										
TO-17 MS	HR01101		1						500	1	Carbopak charcoal
NIOSH 2505	HR01102		1						500	2	Porapak Q (SKC 226-115)
NIOSH 2529	HR01103		1						500	3	XAD-2 (SKC 226-117)
OSHA ID200	HR01104		1						500	4	100/50 mg Carbon Bead (SKC 226-80)
TO11	HR01105		1						500	5	DNPH Silica Gel (SKC 226-119)
	Moisture		1						500	6	TOTAL
	Excess								100	7	BLOCKED
	Excess								100	8	BLOCKED
	Excess								200	9	BLOCKED
	Excess								200	10	BLOCKED
	Excess								200	11	BLOCKED
	Excess								200	12	BLOCKED
	Excess								2000	13	Excess

<u>Series – 1412-124 HR-a</u>

Mold Making and Storage Digital Mold Making and Storage Emissions test Process Instructions

A. The Experiment:

a. Measure total selected emissions from the making of 4-on irregular gear molds with the ExOne S15 mold printing machine.

B. Materials:

- **1.** Prometal FS001 Sand
- 2. Prometal RCT Binder FB001-EU
- 3. Prometal RCT Activator FC001-EU

C. Machine setup.

- 1. The ExOne S15 machine is to be operated by trained personnel only.
- **D.** Mold making and storage test: 2 Boxes of 4 molds (1 cope, 1 drag) each. At least six (6) emissions samples will be taken for each box.
 - 1. Adjust the air flow rate so that all emissions are captured by the emissions team.
 - 2. Attach the emission sample train to the gas-purge-fugitive sample pipe.
 - **3.** Begin monitoring with the THC.
 - 4. Change sampling tubes in between molds per the sampling plan.
 - 5. After the print job has finished continue sampling for 1 hour.
 - 6. Empty and clean the machine, mate and wrap the molds for pouring, cooling and, shakeout tests. Record mold weight.

Tom Fennell Process Engineer

APPENDIX B DETAILED DIGITAL PRINTING PROCESS PARAMETERS

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	Deta	lied Proces	ss Data - I e	SI HKa			
Date	6/21/2007	6/21/2007	6/21/2007	6/21/2007	6/21/2007	6/21/2007	6/21/2007
Emission Test No.	HR001	HR002	HR003	HR004	HR005	HR006	HR007
Sample Time, min	500	1005	1538	1016	09	2115	500
Total Printed Sand Weight During Run, Ibs.	289.5	579.0	868.5	579.0	0.0	1158.0	289.5
Printed Binder % BOS	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Printed Binder% Actual	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Printed Binder Weight	4.3	8.6	12.8	8.6	0.0	17.1	4.3
Total Stored Sand Weight During Run, Ibs.	0.0	289.5	579.0	868.5	1158.0	1158.0	0.0
Stored Binder Weight During Run	0.00	4.28	8.56	12.83	17.11	17.11	00.00

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CRADA PROTECTED DOCUMENT

Technikon # 1412-124 HRA JANUARY 2008

JANUARY 2008

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Detailed Digital Process Parameters - Test HRa

[Global]	
Manufacturer	PROMETAL RCT
Model	S15
Name	5018
Indiffe	5/21/2007 12:57
Job Completion	5/23/2007 0:15
Slicos	100/
Hoight	559.2 mm
	5/22/2007 0.15
Lasi Enity	5/23/2007 0.15
[Build Time]	
Elansed	1 11.17.26
Romaining	0 00:00:00
Estimatod	5/23/2007 0:15
Louinatea	5/25/2007 0.15
[Job Parameters]	
Print Resolution	x: 0.100 mm y: 0.127 mm z: 0.280 mm
Print Pastor	v 1 v 1
Print Offset	x [·] -0.100 mm y [·] -0.150 mm
Print Sneed	0.50 m/s
Pacastar Speed	4200 PPM
Print Head Mayo Form	12 ms 22 ms 22 ms
Initial Height 7	-0.160 mm
	-0.100
Start Layer	1
Stup Layer	1774
Activator Dosage	U.34%
Input File Path	
Input File	Build box for gear.r3d
[Matorial Lleage]	
[Material Usage]	20 470/
Activator Level Delore	38.47%
ACTIVATOR IEIT	37.00%
Binder Level belore	20.41 L
Binder lett	11.28 L
Cleaner Level before	19.92 L
	10.70 L
Build Dimensions	U.705 M^3
[Lover Time]	
[Layer Time]	51.0 s
Last	51.0 S
Average	03.0 5
SHUTLESL	12.3 5
LUNGESI	81.0 S
TUIAI	1, 11:06:22
	1994
Amount	99.00%
[Depending Time]	
[Recoaling Time]	20 / *
Last	20.0 S
Average	18.2 S
Shortest	12.0 s
Longest	35.2 s
Total	0, 10:21:26
Quantity	1994
Amount	29.00%
[Printing Time]	
Last	30.2 s
Average	44.0 s
Shortest	0.0 s
Longest	51.0 s
Total	1, 00:40:40
Quantity	1994
Amount	69.00%

ivieanino rimer		
Last	12.2 \$	
Average	12.5 s	
Shortest	10.1 s	
Longest	26.4 s	
Total	0.01:20:56	
	460	
Amount	407	
AIIIUUIII	4.00 %	
[Hardware Dialog	Time]	
Last		
Average		
Shortest		
Longest		
Total		
Quantity		
Amount	0.00%	
[Idlo Timo]		
LdSI		
Average		
Shortest		
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lotal		
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Amount	0.00%	
DMaiting for Close	ing Completion Time]	
[waiting for Clean		
Lasi	1.5 \$	
Average	3.3 S	
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	0.2 5	
Longest	0.2 S	
Longest Total	0.2 S 11.8 S 0, 00:26:31	
Longest Total Quantity	0.2 S 11.8 S 0, 00:26:31 469	
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Longest Total Quantity Amount [Error Time] Last Average Shortest Longest Total Quantity Amount [Printhead Recover	0.2 s 11.8 s 0, 00:26:31 469 1.00% 0.0 s 0.0	
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Longest Total Quantity Amount [Error Time] Last Average Shortest Longest Total Quantity Amount [Printhead Recover Last Average Shortest	0.2 s 11.8 s 0, 00:26:31 469 1.00% 0.0 s 0.0	
Longest Total Quantity Amount [Error Time] Last Average Shortest Longest Total Quantity Amount [Printhead Recover Last Average Shortest Longest	0.2 s 11.8 s 0, 00:26:31 469 1.00% 0.0 s 0.0	
Longest Total Quantity Amount [Error Time] Last Average Shortest Longest Total Quantity Amount [Printhead Recove Last Average Shortest Longest Total	0.2 s 11.8 s 0, 00:26:31 469 1.00% 0.0 s 0.0	
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Mass properties of Mold Cope (Part Configuration - Default) Output coordinate System: -- default --Density = 1.414080 grams per cubic centimeter Mass = 67826.355021 grams Volume = 47964994.599640 cubic millimeters Surface area = 1211738.613073 millimeters^2 Center of mass: (millimeters) X = 311.126285 Y = 61.299676Z = -330.653962Principal axes of inertia and principal moments of inertia: (grams * square millimeters) Taken at the center of mass. Ix = (-0.000001, 0.000040, 1.000000) Px = 2212567717.934013 Iy = (1.000000, 0.000000, 0.000001)Py = 2501637741.494572 Pz = 4533279975.100127 Iz = (0.000000, 1.000000, -0.000040)Moments of inertia: (grams * square millimeters) Taken at the center of mass and aligned with the output coordinate system. $\begin{aligned} Lxx &= 2501637741.494247 \quad Lxy &= -0.000000 \quad Lxz &= -307.619030 \\ Lyx &= -0.000000 \quad Lyy &= 4533279971.342672 \quad Lyz &= 93380.823222 \end{aligned}$ Lzx = -307.619030 Lzy = 93380.823222 Lzz = 2212567721.691807 Moments of inertia: (grams * square millimeters) Taken at the output coordinate system. lxx = 10172099423.281399 lxy = 1293580215.411739 lxz = -6977646010.592954 lyx = 1293580215.411739 lyy = 18514435613.342434 lyz = -1374677714.712122 Izx = -6977646010.592954 Izy = -1374677714.712122 Izz = 9032997132.973963

Mass properties of Mold Drag (Part Configuration - Default)

Output coordinate System: -- default --

Density = 1.4140803 grams per cubic centimeter

Mass = 69329.8992473 grams

Volume = 49028261.0935812 cubic millimeters

Surface area = 1365119.8691779 millimeters^2

Center of mass: (millimeters) X = 311.1517140 Y = 75.6612333Z = -330.3862466

Principal axes of inertia and principal moments of inertia: (grams * square millimeters) Taken at the center of mass.

IX = (0.0029442, 0.0003069, 0.9999956)	Px = 236586/909.99/75/9
Iy = (0.9999957, -0.0000034, -0.0029442)	Py = 2642707244.9926186
Iz = (0.0000025, 1.0000000, -0.0003069)	Pz = 4791756988.1892109

Moments of inertia: (grams * square millimeters)

Taken at the center of mass and aligne	ed with the output coordinate s	system.
Lxx = 2642704845.3246765	Lxy = -5201.5122192	Lxz = 815060.2515634
Lyx = -5201.5122192	Lyy = 4791756759.7094011	Lyz = 744467.9464428
Lzx = 815060.2515634	Lzy = 744467.9464428	Lzz = 2365870538.1455202

Moments of inertia: (grams * square millimeters)

Taken at the output coordinate system.

Ixx = 10607302469.9084030Ixy = 1632167775.0493612Ixz = -7126315701.5973091Iyx = 1632167775.0493612Iyy = 19071668075.3109890Iyz = -1732324897.7181077Izx = -7126315701.5973091Izy = -1732324897.7181077Izz = 9474959194.0583992

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APPENDIX C CONTINUOUS EMISSION CHARTS

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APPENDIX D ACRONYMS AND ABBREVIATIONS

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Acronyms & Abbreviations

AFS	American Foundry Society
ARDEC	(US) Army Armament Research, Development and Engineering Center
BO	Based on ().
BOS	Based on Sand.
CAAA	Clean Air Act Amendments of 1990
CARB	California Air Resources Board
CERP	Casting Emission Reduction Program
CFR	Code of Federal Regulations
CISA	Casting Industry Suppliers Association
CRADA	Cooperative Research and Development Agreement
DOD	Department of Defense
DOE	Department of Energy
EEF	Established Emission Factors
EPA	Environmental Protection Agency
ERC	Environmental Research Consortium
FID	Flame Ionization Detector
GC/MS	Gas Chromatography – Mass Spectrometry
HAP	Hazardous Air Pollutant defined by the 1990 Clean Air Act Amendment
HC	Hydrocarbon
Ι	Invalidated Data
I Lb/Lb	Invalidated Data Pound per Pound of Binder used
I Lb/Lb Lb/Tn	Invalidated Data Pound per Pound of Binder used Pound per Ton of Metal poured
I Lb/Lb Lb/Tn LOI	Invalidated Data Pound per Pound of Binder used Pound per Ton of Metal poured Loss on Ignition
I Lb/Lb Lb/Tn LOI NA	Invalidated Data Pound per Pound of Binder used Pound per Ton of Metal poured Loss on Ignition Not Applicable; Not Available
I Lb/Lb Lb/Tn LOI NA ND	Invalidated Data Pound per Pound of Binder used Pound per Ton of Metal poured Loss on Ignition Not Applicable; Not Available Non-Detect; Not detected below the practical quantitation limit
I Lb/Lb Lb/Tn LOI NA ND POM	Invalidated Data Pound per Pound of Binder used Pound per Ton of Metal poured Loss on Ignition Not Applicable; Not Available Non-Detect; Not detected below the practical quantitation limit Polycyclic Organic Matter
I Lb/Lb Lb/Tn LOI NA ND POM QA/QC	Invalidated Data Pound per Pound of Binder used Pound per Ton of Metal poured Loss on Ignition Not Applicable; Not Available Non-Detect; Not detected below the practical quantitation limit Polycyclic Organic Matter Quality Assurance/Quality Control
I Lb/Lb Lb/Tn LOI NA ND POM QA/QC RCT	Invalidated Data Pound per Pound of Binder used Pound per Ton of Metal poured Loss on Ignition Not Applicable; Not Available Non-Detect; Not detected below the practical quantitation limit Polycyclic Organic Matter Quality Assurance/Quality Control Rapid Casting Technology
I Lb/Lb Lb/Tn LOI NA ND POM QA/QC RCT SO ₂	Invalidated Data Pound per Pound of Binder used Pound per Ton of Metal poured Loss on Ignition Not Applicable; Not Available Non-Detect; Not detected below the practical quantitation limit Polycyclic Organic Matter Quality Assurance/Quality Control Rapid Casting Technology Sulfur Dioxide
I Lb/Lb Lb/Tn LOI NA ND POM QA/QC RCT SO ₂ TA	Invalidated Data Pound per Pound of Binder used Pound per Ton of Metal poured Loss on Ignition Not Applicable; Not Available Non-Detect; Not detected below the practical quantitation limit Polycyclic Organic Matter Quality Assurance/Quality Control Rapid Casting Technology Sulfur Dioxide Target Analyte
I Lb/Lb Lb/Tn LOI NA ND POM QA/QC RCT SO ₂ TA TEA	Invalidated Data Pound per Pound of Binder used Pound per Ton of Metal poured Loss on Ignition Not Applicable; Not Available Non-Detect; Not detected below the practical quantitation limit Polycyclic Organic Matter Quality Assurance/Quality Control Rapid Casting Technology Sulfur Dioxide Target Analyte

Technikon # 1412-124 HRa

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ТНС	Total Hydrocarbon Concentration
US EPA	United States Environmental Protection Agency
USCAR	United States Council for Automotive Research
VOST	Volatile Organic Sampling Train
WBS	Work Breakdown Structure