Measurement of Condensate- and Smoke-Causing Emissions from Automotive Paints and Sealers

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Two major problems that periodically arise during the surface coating of automobiles are oven plume opacity (smoke that violates local opacity ordinances) and oven condensate that can drip on cars and leave an oily residue. Both of these problems are caused by the evaporation of semi-volatile organic compounds in bake ovens. A new test procedure has been developed to standardize the analysis and reporting of condensate/smoke-causing compounds that are emitted from paint, sealer, and coating materials when they are baked. Use of this test will allow identification and quantification of potential sources of condensate, smoke, and opacity in the laboratory. The information is essential to material suppliers and formulators, and to users who prescreen materials in order to avoid costly problems in production.

INTRODUCTION

Automotive assembly plants typically apply multiple coatings as well as various sealers and adhesives, all of which are baked in large ovens. Each of these ovens may be 150-700 feet long and exhaust hot air at 10,000-30,000 scfm from one or more stacks. Emissions from these stacks consist primarily of volatile and semi-volatile organic compounds that are used as solvents and plasticizers, as well as compounds released during curing reactions. Some oven exhaust stacks are abated to control emissions and odor. Unabated oven exhaust stacks can have visible plumes, giving rise to potential opacity concerns. Most states have regulations prohibiting opacity excursions. For example, states such as Michigan and Ohio with many automotive assembly plants, generally limit plume opacity to 20% for a six-minute average,[1,2] and Maryland prohibits any visible plume. These regulations are generally based on the control of particulate matter and may be process—and even plant—specific.

Plume opacity is generally caused by fine aerosols that scatter light, reducing visibility through the plume. For exhaust stacks from bake ovens, the aerosols in the plume consist mostly of condensed organic compounds and in some cases water. These organic compounds are often plasticizers and other low volatile compounds in the coatings and sealers, or bake products that have sufficient vapor pressure at oven temperatures to evaporate, but low enough vapor pressures at ambient temperatures, condense and aerosolize in the plume. Opacity arising from the aerosols is a function of all of the parameters that affect light scattering, including mass of the aerosol, its size and optical properties, local meteorology and plume dimensions, and solar angle with respect to the plume and the observer.[3,4] Actual opacity is determined by visual observations and cannot be quantitatively predicted from aerosol data alone. The standard method for measuring opacity uses EPA Reference Method 9, which calls for a trained observer to observe the plume under specific conditions.[5] Opacity depends on many variables, most of which vary with time and local conditions. Therefore, opacity cannot be completely determined in the laboratory, but it can be inferred from aerosol properties and is clearly related to the mass of condensable emissions.

A related problem is smoke inside the plant, either inside an oven or in air exiting an oven into the main plant environment. This is the same phenomenon as opacity and is also caused by condensing organic compounds forming fine aerosols that scatter light. Like opacity, smoke depends on local plant conditions, but can be inferred from emissions levels.

One of the most serious problems resulting from bake oven emissions in the automotive industry is severe condensation. When vapors of semi-volatile emissions contact surfaces that are below their dew points, they will partly condense. This can occur on room temperature surfaces near oven exits, or on inside oven surfaces (e.g., doors and expansion joints) that are cooler than the oven air. Drops of oily condensate can range from a minor nuisance requiring more frequent maintenance, to more severe problems that may cause the shut down of the coatings line.

Information on emissions of semi-volatile compounds from paints, coatings, and sealers is the best predictor for condensation, smoke, and opacity. Previously, there were no quantitative test methods to measure condensation/smoke-causing emissions. The nearest technique is the so-called smoke test in which one simply heats a sample under an inverted funnel and looks for smoke. The test is not contained, has no control on air flow and circulation, and is not quantitative. There are standard tests for determining particulate emissions from stacks, but they are not directly suitable for the laboratory. EPA Reference Method 5,[6] for example, is designed strictly for stacks with flow rates and sample sizes at least four orders of magnitude greater than those needed in the laboratory. Additionally, it defines particulate emissions as the mass that is transported through a heated sample tube and retained on a heated filter (usually at 120°C). Most of the condensate/smoke-causing emissions from paints and sealers are in the vapor phase at

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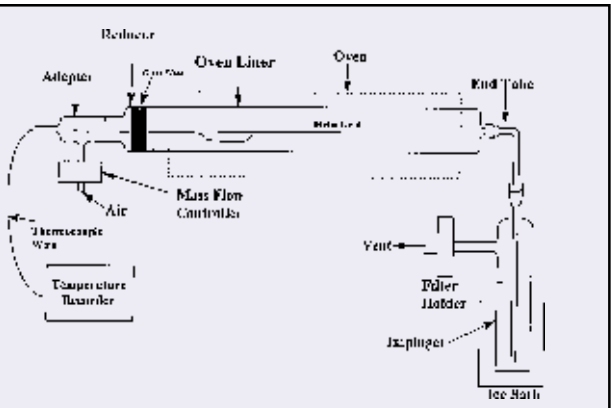

Figure 1—Schematic of the bake oven set-up.

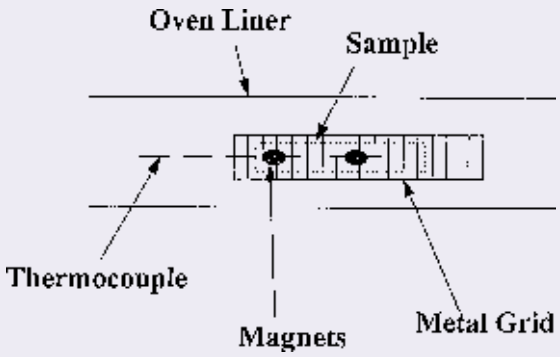

Figure 2—Schematic of metal grid in oven liner.

120°C and would not be retained on a heated filter or measured as aerosol.

This report describes a new test procedure[7] that allows bake emissions from paints, sealers, and other automotive coating products to be quantified easily in the laboratory in order to avoid any potential problems in production where remedies are often difficult and expensive. The procedure was developed to standardize the analysis and reporting of the mass of the emissions from paint, sealer, and coating materials during bake in an oven as a function of time and temperature. Originally developed for automotive use, the test can easily be applied to most other types of coatings. In this procedure a small sample of the test material is baked in a tube oven while a stream of clean air sweeps the emissions out of the oven and into a cold impinger followed by a filter. The emissions collected by the impinger and filter are analyzed for total mass and can also be further analyzed for composition. This procedure specifically addresses the condensate/smoke-causing part of the oven emissions, which includes solids and semi-volatile constituents. Emissions of volatile compounds may not be completely quantified by this procedure.

TEST EQUIPMENT

Bake Oven Set-up: The schematic of the set up for baking and collecting the emissions from a given sample material is shown in *Figure* 1. A Thermolyne 21135 furnace or equivalent is used to bake the sample material. The furnace is a cylindrical unit equipped with the temperature control in the range of 100° to 300°C. A custom Pyrex tube liner (2 in. OD, 1.5 in. ID, and 22 in. length, 50/50 ground glass joint on one end, and 12/5 ball joint on other end) is placed snugly into the furnace. A 50/50 to 24/40 reducer is used to connect a 24/40 adapter with inlet hose connection to the liner. Bottled air (hydrocarbon free) is connected to a flow controller that meters the airflow to the adapter. A glass wool plug is placed at the adapter-liner junction to smooth out the air flow. To eliminate heat loss and condensation and improve temperature stability, the inlet assembly is heated and insulated.

The sample is placed in the middle of the oven liner on top of a metal grid (1.25 in. × 6 in.). The metal grid rests on the inner wall of the oven liner (see *Figure* 2). A thermocouple wire (K-type) is passed through the adapter and placed in contact with the under side of the metal grid or the sample panel/container. A pair of magnets is used to hold the thermocouple in place. The thermocouple is connected to a temperature recorder (see *Figure* 1).

The exhaust end of the oven liner is connected through a 12/5 female ball connection to an L-shaped adapter (end tube), which is then connected to a 25 ml-midget impinger. The oven end assembly up to the impinger is fully insulated (heating tape can be used). The oven exhaust bubbles through the impinger, which is placed in an ice-water bath, and then passes through a short tube into a filter holder assembly. The filter holder houses a 47-mm filter (Pallflex, type T60A20). The air out of the filter flows into the exhaust hood.

Miscellaneous: Additional equipment and laboratory items required for testing include small pieces of stiff wire (or paper clips), 50 × 9 mm sterilized disposable petri dishes, 20-ml screw top vials, film thickness gauge (CMI CGX-A2 or equivalent), four place balance, desiccator aluminum evaporating dish, 47-mm filter (Pallflex, type T60A20), and analytical grade methanol.

Sample Preparation

Electrocoat and Liquid Coatings: For testing of electrocoat material (ELPO), arrangements can be made with a supplier to coat preweighed cold-roll steel panels (panel weight = Wi) of size 1.5 in. × 4 in. with the ELPO material (the bath conditions and the film thickness should match the actual production conditions). The coated panels are then used for emissions testing.

Preweigh the metal grid and two small pieces of stiff wire or paper clips (risers) (W2) and place the risers on the grid. With as little touching as possible, place the panel over the risers on the support plate (note that the ELPO-panels are coated both sides). Weigh the assembly (Wf). The initial sample weight (Wsi) is then:

$$Wsi = Wf - Wi - W2$$

For testing of liquid coatings (primer, basecoat, or clearcoat), arrangements can be made with the supplier to coat panels (1.5 in. × 4 in.). They can also be prepared in the lab by spraying or by placing the coating material on the panel and smoothing it out to the desired thickness using the simple panel-slide test unit. The coated area should be at least one inch wide by three inches long at thickness comparable to the production setting. The panel is weighed before (Wi) and after coating (Wf). The initial sample weight is:

$$Wsi = Wf - Wi$$

If the initial weight of the cold-rolled steel panel is not available, then the weight of the cured sample (Wsf) can be estimated using the measured film thickness, coated surface area, and density of the coating on the panel. The initial sample weight can then be estimated by dividing the non-volatile fraction of the coating, or by adding the measured weight loss of the sample during bake (ΔWs) to Wsf, i.e.:

$$Wsi = Wsf + \Delta Ws$$

Powder Paint and Sealers: For powder paint, the sample is tested using an aluminum dish. Trim off the sides of an aluminum weighing dish so that it will fit inside the glass liner of the furnace. Weigh the dish (Wi). The powder sample is then sprinkled in the dish and smoothed out to cover at least a 1.5 in. × 2 in. square area at the thickness that is used in production plants (about 3 mils for cured powder primer). The dish is then weighed again (Wf). The amount of the powder sample can be estimated by calculating the mass needed to cover the area of the desired thickness.

For a sealer that comes as paste, place about 1.0 gram of the sample in a preweighed aluminum dish (Wi). The sample is then smoothed out to cover at least a 1.5 in. × 2 in. square area. The dish is then weighed again (Wf).

For a sealer that comes in solid form, cut a 1.5 in. × 2 in. piece and place it in an aluminum dish. Weigh the dish before (Wi) and after (Wf). The initial sample weight is:

$$Wsi = Wf - Wi$$

Test Procedure

Initial Preparations:

- Make sure all the components of the system are clean; they must be cleaned before each run.
- Turn the oven on and set to desired temperature. Allow one hour for temperature stabilization.
- Preweigh the bottom half of a petri dish, then set the Pallflex filter in the dish and place it uncovered in the desiccator for one hour. The filter is then weighed with the petri dish and placed in the filter holder. Care must be taken to ensure that both parts of the filter holder are lined up correctly before tightening, or leaks will occur nullifying the filter data.
- Fill the impinger with 20 ml methanol and place it in the ice bath. Clamp the impinger inlet to the exhaust end of the oven glass liner and the impinger outlet to the filter holder. The impinger can also be run dry (no methanol).
- Turn on the air and set the flow rate at 1 L/min. Verify that there are no leaks throughout the system. Air flow rates of 3 L/min can be used with a dry impinger.

Emissions Test: Open the adapter-inlet assembly. With as little touching as possible, place the coated panel on the metal grid over the risers (note that the ELPO panels are coated both sides). The sample in an aluminum dish is simply placed on the metal grid. With a pair of magnets, attach the thermocouple to the sample container or to the coated panel underside (near the middle). For ELPO panels, place the thermocouple in contact with the grid. Using tongs, place the metal grid in the center of the oven. Push the metal grid into the furnace using a glass rod or similar tool until the sample is centered in the oven. Close the adapter-inlet assembly.

Set the timer for 25 min and begin recording the temperature of the sample. After 25 min, open the oven inlet assembly and remove the metal grid with the sample. Replace the inlet, set the temperature of the oven to 200°C, and flush the system with the purified air for 20 min. (A 10-min flush is sufficient with 3 L/min air flows). Leave the sample to cool for 60 min in the desiccator.

After the 20-min flush, remove the filter and leave it to cool in the desiccator for four hours. Disconnect the impinger and the end tube. While the end tube is cooling, pour the impinger solution into a 20-ml vial. (When a dry impinger is used, rinse the impinger two to three times with a total of about 10 ml methanol and pour this solution into a 20-ml vial.) Rinse the end tube twice with 2 ml methanol and into the impinger. Pour the impinger solution (4 ml) into the 20-ml vial. Again use 2 ml of methanol to rinse the end tube into the impinger and add this rinse to the 20-ml vial. Finally, use additional methanol to rinse the impinger to bring the total solution volume in the vial to 20 ml. Keep 5 ml of the vial solution for analytical speciations (if desired) and retain the remaining 15 ml for mass emissions analysis.

Weigh the baked sample/panel (Wff). The weight of the sample after bake is then:

$$Wsf = Wff - Wi$$

For the cold-rolled and wet coatings, measure the cured film thickness using a calibrated film thickness gauge. The results are reported in mils.

Analysis

Impinger: 15 ml of the impinger solution that was collected in the 20-ml vial is placed in a 50-mm aluminum bowl that has been desiccated for a minimum of one hour and weighed. The sample is allowed to sit in a hood at 20°C for 24 hr. The sample is then desiccated for about one hour and weighed. The increase in the weight of the bowl represents the mass of solids collected in the vial solution (Mv). This number multiplied by 4/3 (or the inverse of the fraction of total solution that was evaporated) gives the solids collected in the impinger and the end but (M1).

Filter: The filter is returned to the petri dish that was used in the initial weighing, then desiccated for a minimum of four hours. The filter is then weighed, and the increase over its initial weight gives the mass of solids collected on the filter (M2).

Total Emissions: The smoke-causing emissions from the sample (Mt) is the sum of the solids collected in the impinger as well as on the filter:

$$Mt = M1 + M2$$

The emissions as wt% of the sample are then given by:

$$Mt1 = Mt/Wsi * 100$$
$$Mt2 = Mt/Wsf * 100$$

Where Mt1 and Mt2 are based on the initial sample weight (wet) and the final weight (baked), respectively.

Test Matrix

A given sample material must be tested for emission a number of times to determine the effects of bake temperature and time. The following tables list the required test matrix for ELPO, powder/liquid primer, topcoats, and sealers.

The test matrix of ELPO panels is given in *Table* 1. ELPO panels should be run at three different temperatures based on the bake window specified for the material: the lowest temperature (Emin), maximum temperature (Emax), and the midpoint temperature (Emid). Four ELPO panels are run at each temperature. After taking all necessary measurements, these panels then go through a second bake for 25 min. The tempera-

Table 1—Test Matrix for ELPO Panels

	First Bake at ELPO Oven Temperatures	Second Bake at Primer Oven Temperatures
ELPO	Emin (4)*,+	Pmid (2), Pmax (2)
	Emid (4)	Pmid (2), Pmax (2)
	Emax (4)+	Pmid (2), Pmax (2)

* Number in brackets denotes the number of runs at the temperature.
\+ Prepare 6 panels instead of 4 if going also for *Table* 2 test matrix.

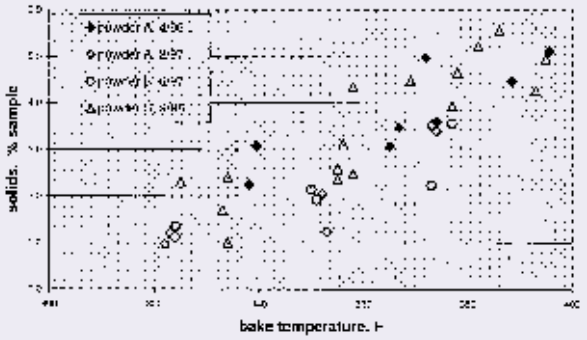

Figure 3—Solid emissions from some powder primers used in the automotive industry.

ture for the second bake is defined by the operating window for powder or liquid primer that is going to be used with the ELPO. The rebake is done at the primer oven midpoint (Pmid) and maximum (Pmax) temperatures. The 12 ELPO panels, which were baked at Emin, Emid, and Emax in the first bake, are rebaked at Pmid and Pmax with two runs per temperature.

The test matrix for powder/liquid primer is given in *Table* 2. The primer is tested at three temperatures based on the operating window for the primer: minimum (Pmin), midpoint (Pmid), and maximum (Pmax). The primer is also prepared over ELPO panels that have been baked at Emin and Emax. These panels are then baked for 25 min at Pmax.

Topcoats (basecoats, liquid, and powder clearcoats) should be tested individually and over the recommended ELPO and prime coats. The test matrix for each topcoat is given in *Table* 3. The topcoat is tested at three temperatures based on the operating window for the final topcoat bake: minimum (Tmin), midpoint (Tmid), and maximum (Tmax). The topcoat is also prepared over panels with ELPO and prime that have been baked at Emin/Pmin and Emax/Pmax. The panels are then baked for 25 min at Tmax.

Each basecoat and clearcoat first should be tested independently. Basecoats should be sprayed onto the panel and then flashed under appropriate conditions before being placed in the tube oven. Clearcoats should also be sprayed and allowed to air flash. Results should be reported in terms of weight of cured film, the most accurate measure of the amount of coating applied. Film build should also be reported.

Additional tests should be run by applying ELPO, prime, basecoat, and clearcoat at the appropriate film builds, cured at the minimum and maximum temperatures for ELPO and prime, and at the maximum temperature for topcoat. There is no need to test basecoats alone over ELPO and prime (without clearcoat).

The test matrix for sealers is given in *Table* 4. Sealers that are applied in the body shop (before paint) are tested at Emin, Emid, and Emax; the samples that are baked at Emin and Emax are then rebaked at Pmax for 25 min. Sealers that are applied in the paint shop (after ELPO) are baked at Pmin, Pmid, and Pmax. Sealers that are applied after the primer oven are baked at three temperatures based on the operating window for the sealers: minimum (Smin), midpoint (Smid), and maximum (Smax) temperatures.

Table 2—Test Matrix for Powder/Liquid Primer

Bake by Itself	Over ELPO Baked at Emin	Over ELPO Baked at Emax
Pmin (2)		
Pmid (2)		
Pmax (2)	Pmax (2)	Pmax (2)

Table 3—Test Matrix for Topcoats

Bake by Itself	Over ELPO Baked at Emin and Prime at Pmin	Over ELPO Baked at Emax and Prime at Pmax
Tmin (2)		
Tmid (2)		
Tmax (2)	Tmax (2)	Tmax (2)

Table 4—Test Matrix for Sealers

Body Shop Sealers		Sealers after ELPO	Sealers after Primer
First Bake at ELPO Oven Temp.	Second Bake at Primer Oven Temp.	Bake at Primer Oven Temp.	Bake at Sealer Oven Temp.
Emin (2)	Pmax (2)	Pmin (2)	Smin (2)
Etar (2)		Ptar (2)	Star (2)
Emax (2)	Pmax (2)	Pmax (2)	Smax (2)

Reporting

The report should contain the following:

(1) Date and time of testing
(2) Name of laboratory/supplier conducting the test
(3) Material MSDS, identification codes, and date of material production
(4) A summary paragraph reporting the range of Mt1 and Mt2 measured during different bakes

In addition the report should include:

(1) All the raw data and calculated emissions data
(2) Oven temperature profile (thermocouple recorder)
(3) Any general observations of the experiment (spills, problematic equipment, etc.)
(4) Appearance of the emissions collected from the impinger (in the bowl) and on the filter

Reproducibility

Reproducibility within a lab is a function of the reproducibility of the various critical steps—sample preparation, bake and emissions collection, and analysis—all of which depend on the type of sample. For example, gasket material can easily be cut to within 5%, and powder paint can be sprinkled on a dish with a reproducibility under 1%, but it is difficult to spray an even coat of paint on a small panel with reproducibility under 10%. Even though the results are reported as a fraction of the sample mass, which can be measured very precisely, the amount of sample (actually the thickness or film build) is an important factor affecting the emission rate; so a 10% standard deviation in the sample size often adds a few percent to the overall variation. Sample collection and analysis is generally reproducible to within 10% at

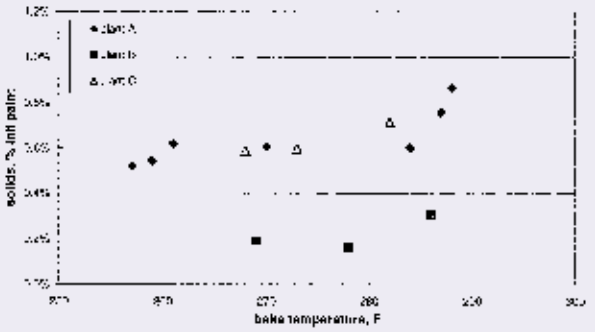

Figure 4a—Solid emissions from basecoats used at three automotive assembly plants.

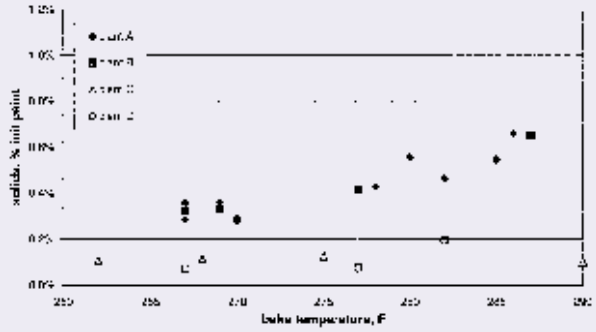

Figure 4B—Solid emissions from clearcoats used at four automotive assembly plants.

the 10 mg level. Our overall emission results (as seen in the next section) generally have a reproducibility better than 15%. (Recovery and reproducibility of individual species will be discussed in a future report on speciation.)

There is as yet very little data on lab-to-lab reproducibility, since we are aware of only one other laboratory so far that has used this procedure. While tests at that lab were not conducted in a way to provide proper statistics, their results agreed well with ours: emissions from an automotive topcoat were within 15%.

RESULTS

To date, this test procedure has been used to characterize emissions from dozens of automotive sealers and coatings, including e-coats, primers, basecoats and clearcoats. Many of these tests were conducted to help solve serious production problems. Since the purpose of this report is to document the test method and not to discuss emissions from actual samples, only a few examples of test results are included here. Most of these examples are early exploratory tests that did not always follow the complete matrix described in the tables. *Figure* 3 shows the results of tests on several powder primers used in the automotive industry. The primers are all from the same supplier. The two "A" powders are different batches of the same formulation; "B" and "C" are slightly different formulations. The figure is included to show the variability of the test method, the amount of semi-volatile emissions from these powders (one to five percent by weight), and the strong dependence of emissions on the bake temperature.

Figure 4 shows the level of emissions from different basecoats used at three automotive plants. For these paints these emission levels are clearly much lower than for powder primers and much less temperature dependent. It is also clear that the basecoat used at plant C has significantly lower emissions than the paints used at plants A and B. Differences in emission levels are even more striking in sealers, as is shown in *Figure* 5, where emissions as a weight fraction of the sample vary by more than an order of magnitude for various sealers used at the same plant.

In general, from the tests that we have run over the past two years, we can conclude:

- Even plasticizers with very low volatility (boiling points > 600°C) can evaporate and cause problems of smoke and condensate, since vapors of these compounds will readily condense as they cool.
- Emission of these high-boiling compounds are often strongly dependent on temperature.
- Compounds that do not completely evaporate or react during the first bake, can be emitted in subsequent bakes.
- Since coatings and sealers from different suppliers can have very different compositions, emissions can vary over a wide range.

Of course, the whole concept of condensable emissions is somewhat arbitrary and methodological. In a plant environment, more vapor may condense in cold air than in warm, and much more condensation can occur on a cold ceiling in winter than on the same ceiling under the summer sun. But it is clear that the test is very useful for comparing emissions from coatings under standard, repeatable conditions, where significant differences between coatings can be determined and related to production conditions. These examples show that, while there is some scatter in the data, significant differences due to formulation and temperature can be seen. The difference between emissions of 0.2% and 0.6% of a coating can mean the difference between a plume that is in compliance with opacity regulations and one that is in violation (or between a clean oven and one in which oily condensate drips all over the freshly painted product).

SUMMARY

We have described a new laboratory test procedure for quantifying semi-volatile emissions from paint and sealer samples as they are heated under controlled conditions in a tube oven. This test procedure was developed specifically to quantitatively determine the condensate/smoke-causing potential of automotive coatings and other materials that are baked during vehicle manufacturing. It

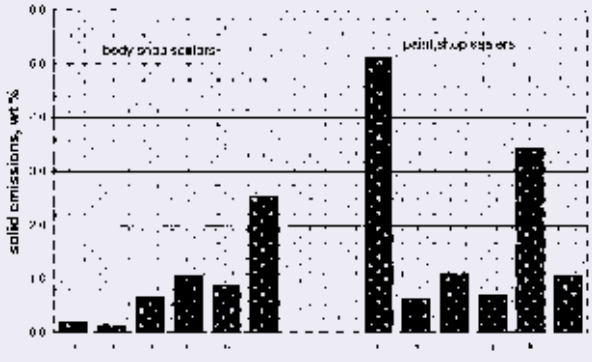

Figure 5—Solid emissions from various sealers used at Plant A.

is also applicable to a wide range of non-automotive coatings.

Results from this test have been used to explain and limit plume opacity from bake oven stacks at several plants. Of even greater importance, test results of emissions from some current and planned coatings were used to help redesign bake oven facilities at several plants in order to eliminate serious condensate problems.

This test does not provide any information regarding emissions of volatile organic compounds or hazardous air pollutants, but additional analyses of the collected emissions (by mass spectroscopy/gas chromatography, for example) can provide detailed information on individual species. The emissions data measured by this test procedure are not sufficient to precisely calculate plume opacity, since opacity also depends on other factors. However, the developed procedure is the single best predictor for assessing a material's potential for condensate, smoke and opacity effects, and provides a unique database for objectively comparing and prescreening different materials.

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