

Measurement of emissions associated with the application of a flammable solvent-based core and mold coating

Introduction

Flammable solvent-based refractory core and mold coatings are used by foundries to reduce the incidence of certain casting defects and to improve as-cast surface finish. The benefits sought through the application of coatings are improved casting quality and the reduction of casting cleaning operations and related costs.

Prior to casting metal against a coated sand mold or core, the liquid carrier contained in the coating must be removed (i.e., the coating must be dried). Liquid coatings containing flammable organic solvents have been chosen by many foundries because these coatings provide the capability to remove the liquid solvent either by air-drying or by simply igniting the coating (light-off).

Coatings containing water as the carrier are also used, but many foundries have chosen in the past not to use these products, since removal of the water from the coating after application requires more attention to the drying stage (time, equipment, energy).

Despite the challenges a foundry may encounter in using water-based coatings, there is more than ample incentive to make this conversion. Clean air regulations in many regions worldwide, already in effect or soon to be introduced, will force foundries to monitor and control emissions from materials used in their plants. VOC (Volatile Organic Compound) emissions associated with solvent-based coatings are among those that will have to be tracked and reported. In certain cases, inability to comply with such emission limits may prevent a foundry from continuing to operate at their required production levels.

This article describes a study performed on behalf of a major steel foundry in North America. The intent of this study was to measure the emissions to the air from a CERAMOL solvent-based core and mold coating during application by brush, within certain waiting time periods prior to light-off, during coating light-off, and over a duration of time immediately following light-off after the flame extinguished. This series was conducted under laboratory conditions which, within the limits of practicality, attempted to simulate the conditions in an operating foundry environment.

Procedural Overview

The laboratory procedure attempted to simulate how a flammable light-off coating is typically applied in a jobbing foundry. While coatings are applied in foundries to cores and molds by a variety of different methods, the means deemed to be simplest, and therefore, best suited for this laboratory investigation was application by brush.

A known amount of a CERAMOL coating was brushed onto a test core specimen and air-dried for a brief period. The coating was then ignited and allowed to burn until the flame extinguished. Following this, the coated core was allowed to cool and stand for an additional period of time. From start to finish of this procedure, compounds emitted were sampled to provide useful information as to their quantity and nature.

Based upon the coating's known composition, the following emission categories were expected and measured:

- VOCs (Volatile Organic Compounds)
- CO₂ (Carbon Dioxide)
- IPA (Isopropyl Alcohol)
- Hydrocarbon solvents

During the actual emission test series, CO (Carbon Monoxide) was not measured. A brief supplementary exercise was performed, sampling CO for a limited number of test runs using a MIRAN analyzer. On average, the CO emission was found to be approximately 5% of the CO₂ emission measured.

Test Materials/Equipment

Test core specimens

Test core specimens (37mm x 82mm x 120mm, typical un-coated weight 500g) were prepared on the day prior to the test series, using Chelford 60 AFS silica sand bonded with 3% sodium silicate binder (grade C112, SiO₂:Na₂O = 2.0:1), based on weight of sand. Specimens were gas-cured with CO₂, then placed into a drying oven @110°C overnight to remove free moisture. Following drying, test core specimens were allowed to cool to ambient temperature and weighed. To determine the level of *free* residual H₂O in the core specimens

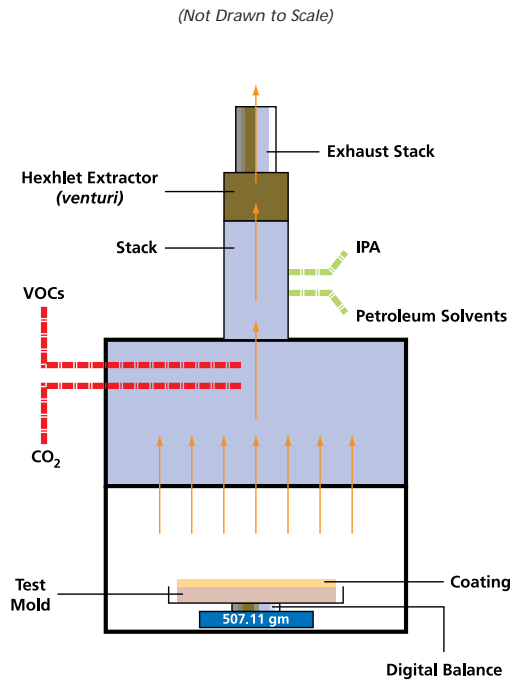


Figure 1: Sampling chamber layout

(from the silicate binder and from possible atmospheric re-hydration during conduct of the testing), following emission tests of coated specimens, un-coated standard (control) specimens were returned to the drying oven for one additional hour. These were cooled and re-weighed. Based on data obtained, a value of 0.6g of residual *free* H₂O was assigned to test core specimens. This moisture level was taken into account in the analysis of test data.

Test coating

The flammable solvent-based CERAMOL coating tested contained a refractory blend of olivine and calcined magnesite. The solvent system was a mixture of isopropyl alcohol and hydrocarbon solvent, with minor fractions of methanol and water. Coating properties and typical composition at application are shown in table 1.

Sampling chamber

A sheet metal construction sampling chamber and a special hexhlet venturi extraction/exhaust head were used to contain and extract emissions (see figures 1–3). The hexhlet device extracted at the rate of 50L/minute. Sampling ports located on the chamber box chimney were used to collect samples to be analyzed for IPA and emissions associated with the hydrocarbon solvent. Probes for sampling of CO₂ and VOCs were inserted through the side of the hood and positioned immediately above the test core.

Air velocity (via portable anemometer) measurements taken in several positions across the front opening of the chamber verified that there was a slight

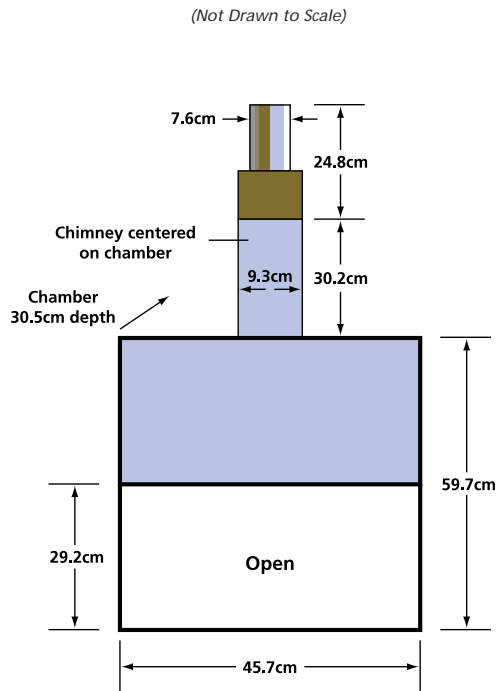


Figure 2: Sampling chamber, front view

inward airflow to the chamber. On average, an inward air velocity of 0.02m/sec. was measured during sampling when the coating was not burning. When the coating was ignited and burning, an air velocity 0.15m/sec. into the chamber during sampling was observed. This inflow of air prevented any of the evolved compounds from exiting the chamber through the front face opening and escaping detection.

Digital balance

For critical weight measurements at various points in each test, a METTLER PC 4400 digital balance (± 0.01 g) was used. The balance was fitted with a special aluminum pan to support the test cores.

CO₂ measurement

This emission was measured using a Foxboro MIRAN infra-red analyzer. Extraction to this device was carried out in the continuous analysis mode, with a sampling flow rate of 7L/min.

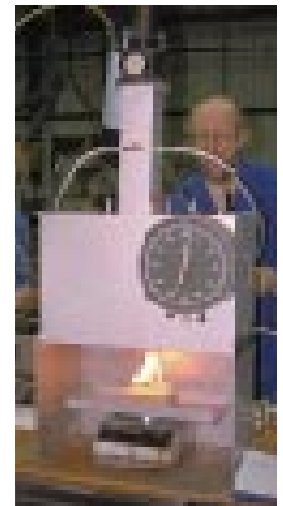


Figure 3

Table 1 – Test coating properties, as-supplied

| Property | As Supplied |
|--|-------------|
| Baume | 44 ± |
| Specific Gravity | 1.277 |
| Solvent (by weight of coating): | |
| IPA (99%) | 34.4% |
| Hydrocarbon Solvent | 9.0% |
| Methanol | 0.4% |
| Water | 0.8% |
| % Solids (refractories, organic resin binder, other) | 55.4% |

Table 2 – Test series description

| Test ID | Coating | Air-drying period (minutes) | Flame-off period (minutes) to flame-out | Standing time (minutes) after flame out |
|---------|-----------------------------|-----------------------------|---|---|
| 1A | Standard | 1 | 1 | 10 |
| 1B | Standard | 1 | 1 | 10 |
| 2A | Standard | 5 | 1 | 10 |
| 2B | Standard | 5 | 1 | 10 |
| 3A* | Standard + H ₂ O | 1 | 1 | 10 |
| 3B* | Standard + H ₂ O | 1 | 1 | 10 |
| 4A* | Standard + H ₂ O | 5 | 1 | 10 |
| 4B* | Standard + H ₂ O | 5 | 1 | 10 |

VOC measurement

VOCs were extracted *en masse* during each phase of testing at the rate of 1L/min. into a Research Engineers GASTEC flame ionization detector (FID) based on a methane/carbon equivalent standard (see figure 4). Data were obtained every 2 seconds from the commencement of each trial to completion. The FID was coupled to a PSION datalogger with a DIGITRON interface, this setup providing converted readings in millivolts (mV). The mV output from the FID was converted to parts per million (ppm) by the PSION datalogger. These ppm readings, in turn, were converted into VOCs evolved in mg. (carbon equivalent).



Figure 4

IPA emission measurement

IPA vapors were sampled during each phase of testing at the rate of 1L/min. through a CASELLA AFC 123 pump. Sampled air was passed through a silica gel adsorption tube. Adsorption tubes were later de-sorbed and analyzed using gas chromatography (quantification) and mass spectrometry (identification) methods. Fresh PVC tubing was used for each test to reduce potential risk of sample contamination and problems that might be caused by condensation of water.

Emissions related to hydrocarbon solvent

These emissions were sampled using a CASELLA AFC 123 pump at the rate of 1L/min. Sampled air was directed through a charcoal adsorption tube. Tubes were later de-sorbed and analyzed using similar methods to those described for IPA

measurement. Fresh PVC tubing was used for each test to reduce any risk of sample contamination and problems that might be caused by condensation of water.

Test Procedure

Coating application procedure overview

At the start of each trial, the test core was placed onto the digital balance, and the initial weight of the un-coated test core was recorded. The digital balance was then tared, after which a cardboard "mask" was set around the test core (6mm clearance between mask and edges of test core) to prevent splashing of coating onto the digital balance during the tests to be conducted. At this point, the coating was applied by brush, (see figure 5) and the cardboard mask removed.

Prior to the start of the emission testing, several trial-run specimen cores were brush-coated to



Figure 5

determine the average wet thickness that could be applied consistently. On average, the immediate wet thickness achieved was 500 microns, with a wet thickness of 230 microns after 1 minute. Wet thickness data were obtained only for reference and were not deemed critical to the conduct of this test series. Coating weight pickup measurements, however, were critical, since emission data obtained were based on the applied coating weight.

Testing / sampling procedure

Listed in table 2 are the tests that were conducted. For each of tests 1A through to 4B, the following procedure was used:

- The uncoated test core was placed onto the digital balance, and the cell was tared to zero.
- The coating mask was applied. Simultaneously, all emission sampling instruments were activated. For each test, 3 "sets" of CASELLA sampling pumps were used so that changeovers required during successive stages of the test could be made quickly. Each set consisted of one pump for IPA emission sampling and one pump for sampling of hydrocarbon solvent emissions. For this phase of the test, the #1 set of CASELLAS was turned *on*. Note that the MIRAN and GASTECH instruments remained *on* from this point through completion of the test.

- CERAMOL coating was applied by brush and the mask was immediately removed. From the digital balance, the weight reading was recorded – wet coating weight applied.
- The coating was allowed to air-dry for the prescribed period of time, namely 1 minute or 5 minutes, after which the #1 set of CASELLA sampling pumps was switched *off*. The weight was again recorded (net weight of applied coating after air-dry period).
- The coating was ignited, while simultaneously switching *on* the #2 set CASELLA pumps. At the end of the coating burn (typically, 1 minute), the #2 set of CASELLA pumps was turned *off* and the weight displayed on the digital balance was recorded (net weight of coating after light-off).
- The #3 set of CASELLA pumps was switched *on* and sampling continued for a further 10 minutes. At the expiration of this period, all sampling instruments were turned *off*. The weight was recorded at this time (dried coating weight).

Using this sampling procedure, the total extraction flow rate through the chamber for each test was 60L/min, namely for the Hexhlet extractor plus all other sampling devices. Therefore, the measurement obtained from each instrument was corrected, based upon that instrument's fraction of the total sampled air extracted from the chamber. For example, since the CASELLA pump sampling IPA had a flow rate of 1L/min., the level of emissions extracted by that pump was assumed to be 1/60 of the total IPA emission, and the measured value, therefore, was multiplied by 60 to obtain the actual emission value.

Over the duration of the testing, approximately 5 hours, ambient temperature averaged 12 - 13°C, with relative humidity of 45%.

Test data acquired

The specimen weight changes at key phases of the tests series were averaged and are shown in figure 6. The actual measurements revealed that, when the coating was ignited after a 1-minute air-dry, most of the IPA and hydrocarbon solvent (70-80%) was "destroyed" in the resultant light-off. Where a longer air-dry period was used (5 minutes), the proportion of solvent destroyed in the flame-off diminished to less than 60%, with a greater fraction being released during the air-drying period. These percentages were relatively unchanged with the addition of 15% water to the coating.

Shown in figure 7 are the average releases of CO₂, IPA, aliphatic hydrocarbons, and toluene. Levels of toluene were not detected during light-off, and averaged only 0.0017gm. during the air-dry stage, and just 0.0010 gm. during the standing phase of

the sampling. In every test, emission of CO₂ (corrected for ambient levels) occurred only during light-off, a by-product of the combustion (destruction) of major portions of the contained organic solvents.

Figure 8 shows the average IPA releases at key phases of measurement. While recovery value analysis accounted for most of the IPA, the residual portion is presumed to have been held in the test cores (beneath surface), even after the completion of the testing. Subsequent weight measurements of the coated test cores after a further 1 hour oven-dry following the expiration of the emission testing showed additional weight loss. Allowing for the known residual H₂O content in the test core, a major portion of this weight loss was attributed to further evaporation of volatile solvents still held in the test core substrate. This observation suggests that a foundry core or mold coating that appears to be dry after light-off may, in fact, still contain amounts of wet solvent that could lead to deleterious casting results.

Figure 9 depicts aliphatic releases associated with the hydrocarbon solvent contained in the test coating. These appear to be consistent with IPA release data, showing the same basic trends. For example, the amount of aliphatic hydrocarbons released during the flame off period is much lower than in the initial air-dry period and subsequent standing period after flame extinguishing, following the same pattern observed in the IPA release results. The aliphatic hydrocarbons referred to in this table are, typically, C7 and C8 paraffins and cycloparaffins. The major components are methylhexanes, heptane, and methylcyclohexane.

VOCs measured ranged from 33.6 - 90.9mg. These data do not appear to be consistent with that shown in figures 6 – 9. This is because these measured VOC data are related to "mg. carbon equivalent," which are calculated on the basis of methane calibration. This is the standard procedure accepted for expressing VOC results in the U.K. to meet national environmental reporting requirements. In absolute terms, the *actual* levels of the VOCs measured are considerably higher. The results obtained via gas chromatography and mass spectrometry analyses shown in figures 6 – 9 are correct.

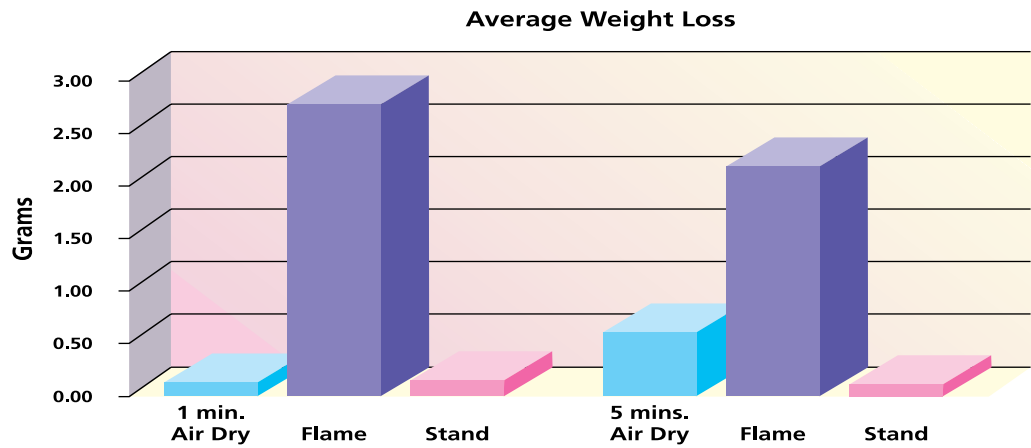


Figure 6: Average weight loss

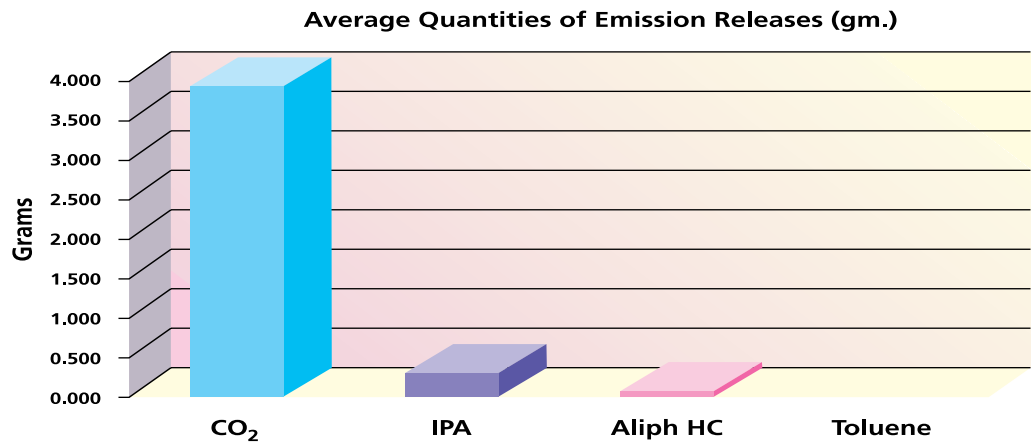


Figure 7: Average quantities of emission releases (gm.)

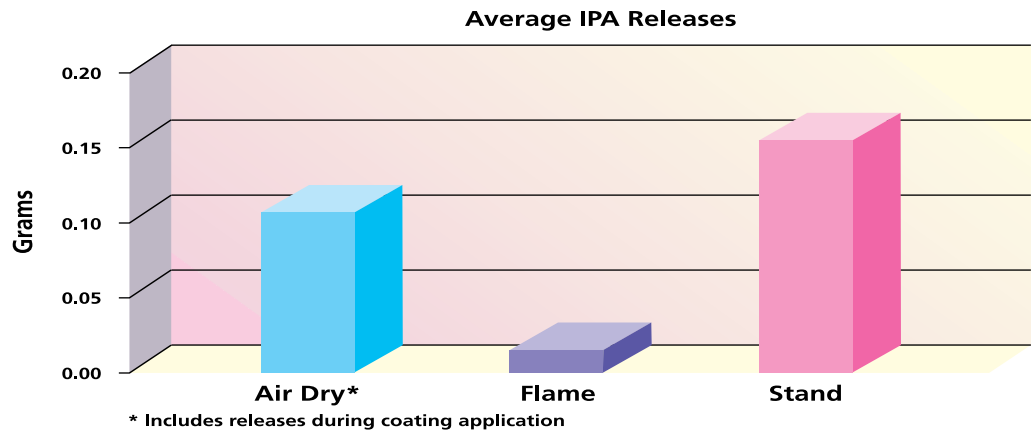


Figure 8: Average IPA releases

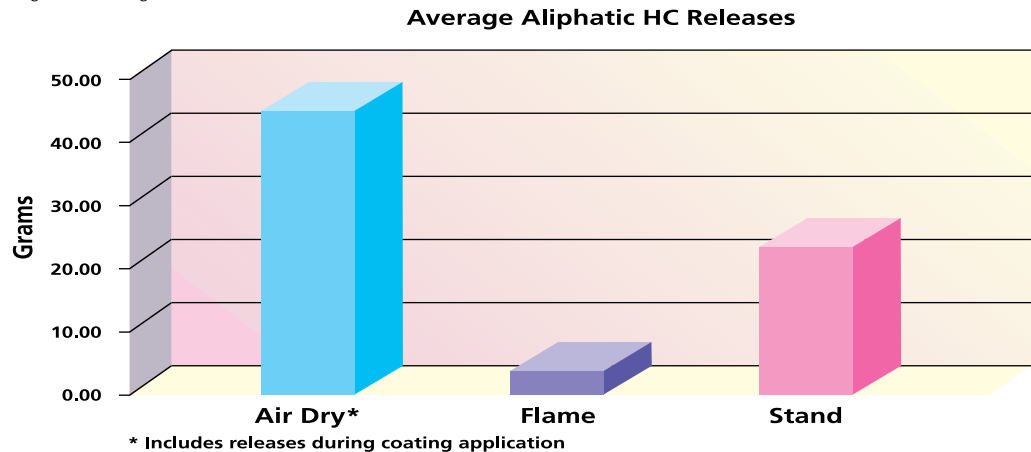


Figure 9: Average Aliphatic HC releases

Key Observations and Conclusions

Based on the work completed in this study, the following key observations were made:

- As long as the test coating was ignited soon after the coating was applied, at least 70% of the volatile organic solvents contained in the coating were destroyed in the flame-off combustion. Increased standing (air-drying) times prior to light-off led to a reduction in the amounts of solvents destroyed;
- Extremely small amounts of volatile solvents (< 1% of original content) were released during flame-off;
- Typically, for relatively short air-drying periods (1 minute), only 7 - 10% of the solvents contained in the coating were released to atmosphere during the process of air-drying, light-off, and standing after light-off. For longer air-drying periods (5 minutes), this figure increased to approximately 15 - 20%.
- Approximately 10 - 20% of the solvent contained in the coating was absorbed by the core and remained there after preliminary air-dry, flame-off, and a 10-minute standing period. This residual solvent could be very slowly released to atmosphere upon further standing.
- In the view of the researchers, the addition of 15% water to the coating appeared to have relatively little overall effect on the test results. Flame colors were observed to have changed somewhat, with an increase in the blue tint of flames compared with the yellow flames present when no water was added.

These findings lead to certain important conclusions:

- Destruction of volatile solvents during the combustion of light-off has been demonstrated and suggests that the total volatile solvent content of the coating should not be considered 100% as a potential VOC emission. Rather, some lesser percentage, 30% of the solvent contained in the coating in this case, should be considered as a potential VOC emission - this assumes that the foundry will use the coating in a manner that parallels this laboratory study.
- The observation that as much as 20% of the contained solvent in the applied coating actually remains in the coated core substrate is a viable explanation for burn-in, burn-on, penetration, and gas defects experienced. The cause of these defects is often assigned to chemically-cured binder practices. This assumption may not always be correct and can lead a foundry to look in the wrong place to resolve a problematic defect. In most foundries, solvent-based coatings are chosen for convenience,

with the perception that the user need only to ignite the coating and the resultant surface will be completely dried. This assumption can be deleterious. On the other hand, a foundry committed to using a water-based coating understands that water is less volatile than a flammable solvent and, as such, foundry personnel will probably exercise greater care in removing the water before casting - as a consequence, casting defects related to "wet" coating are less likely.

- Despite the significant destruction of volatile solvent as a result of light-off combustion, a considerable percentage of the solvent contained in the coating remains (in this case, approximately 30%) and is considered a potential VOC emission. The best environmental compliance strategy for the foundry remains to eliminate potential VOC sources altogether. Conversion to Foseco high-performance water-based coatings (RHEOTEC and HOLCOTE) offers foundries the opportunity to rid themselves of solvent-related VOCs and gain a greater likelihood of meeting increasingly stringent emission limits in the future.

The author expresses appreciation to Foseco Foundry International, Tamworth, England and to the Castings Development Centre, Alvechurch, England for their significant technical contributions to this research.