

DETERMINATION OF CONCENTRATIONS OF ACETIC ACID EMITTED FROM WOOD COATINGS IN ENCLOSURES

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Summary—Twenty-two commercial coatings were chosen, based on their film-forming mechanisms, to study the equilibrium concentrations of volatile organic compounds (VOCs) and their emission rates at steady state. Concentrations of acetic acid (ethanoic acid) and total VOCs were measured using a thermal desorption unit coupled with a gas chromatograph. Almost all coatings released acetic acid, but at different rates. Coatings formed by oxidative polymerization were found to generate a high level of acetic acid at both equilibrium and steady state. The acetic acid equilibrium concentrations from the coatings formed by the other types of mechanism studied tended to be similar to those from red oak, an acidic wood. In a steady-state situation, most of the coatings applied on aluminium or on red oak had acetic acid emission rates lower than that of red oak alone, with the exception of the red oak coated with pigmented films formed by coalescence. The wide range of acetic acid equilibrium concentrations and emission rates for films formed by coalescence is due to the mixture of porous resin, extenders and free acetic acid in the formulations. Consideration should be given to allowing a sufficient drying period (three to four weeks) before using coated enclosures, in order to reduce the VOC concentrations within the enclosures.

Introduction

Wood products and commercial coatings are frequently used in the museum field for display, storage or packing. Although the emission of volatile organic compounds (VOCs) such as acetic acid (ethanoic acid) from wood, and their deteriorating effect on collections, have been well studied [1–7], much less is known about the emission of VOCs from paints and varnishes. Past studies using thermal or normal aging tests have shown that some coatings damage metals and photographic prints [8–15].

In the present study, the equilibrium concentrations and emission rates of acetic acid and total VOCs (TVOC) from coatings and from uncoated and coated red oak samples were investigated. The acetic acid emission rates from coatings and from the red oak samples were used to predict the steady-state acetic acid concentrations in specific leaky enclosures, such as display cases or cabinets.

Film-forming mechanisms

Coatings can be classified according to their film-forming mechanisms. Five common film-forming mechanisms were included in this study: solvent evaporation (e.g., shellac), coalescence (e.g., acrylic emulsion), oxidative polymerization (e.g., alkyd), moisture-cured polymerization (e.g., moisture-cured urethane) and catalyzed polymerization (e.g., two-part systems forming epoxy or urethane resins).

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Oxidative, moisture-cured and catalyzed polymerization form films by cross-linking reactions. Solvent evaporation occurs as a secondary mechanism in all categories. Other types of film-forming mechanism, such as irradiation cross-linking and baking or fusion of resins, are not covered in this paper.

Equilibrium concentration

In the first stage of coating application, VOCs (free or produced from the polymerization) readily evaporate from the film. As the film forms, the emission of VOCs gradually becomes controlled by their rate of diffusion through the film, and their emission rate decreases substantially. If the coated material is put in an airtight enclosure during the drying period, the VOCs in the vapour phase will increase in concentration until they are in equilibrium with the VOCs in the coated surface material.

The equilibrium concentration (C_e) of the VOC and the time taken to reach equilibrium depend on the physical and chemical properties of the VOC-coating-substrate system. Figure 1 shows typical concentration curves for VOCs released by coated and uncoated wood in an airtight enclosure. The shape of the curve depends mainly on whether the coating is emissive and whether the coating contains any blocking or adsorbing components (interactions between VOCs from the coating and the substrate are not considered). With a non-emissive coating on wood (e.g., resin only, with or without

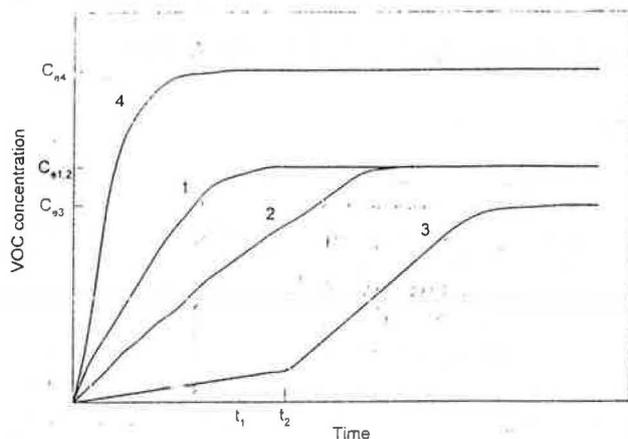


Figure 1 Typical concentration curves for a VOC emitted by coated and uncoated wood in an airtight enclosure.

blocking components such as mica), it will take more time to reach $C_{e1,2}$ (curve 2) than with uncoated wood alone (curve 1). When a non-emissive coating contains adsorbing or reacting components such as calcium carbonate (curve 3), the VOC concentration remains low until equilibrium is reached between the VOC concentrations in the coating resin and in the adsorbing components or until the reacting components are saturated (at time t_2 in Figure 1). Then, the adsorbing or reacting components act as blocking agents, and the equilibrium concentration in the enclosure will be established at a lower level (C_{e3}). With an emissive coating on wood, the equilibrium concentration moves to a higher level (C_{e4}), based on the new VOC-coating-wood system (curve 4). In fact, most coated woods can be emissive, with some components acting as blocking or adsorbing/reacting agents. For determination of C_e , enough time must be allowed to ensure that equilibrium is reached. For example, in Figure 1, the equilibrium concentrations C_{e2} and C_{e3} are not reached at time t_1 for the non-emissive coatings on wood (curves 2 and 3).

The equilibrium concentration can be measured directly by sampling a small volume of air from an airtight test chamber that contains a sample in equilibrium with the vapour phase.

Steady-state concentration

If the coated material is put into a leaky or ventilated enclosure during its drying period, the exhaust air removes some of the VOCs emitted by the material, and a steady-state concentration is established. The steady-state concentration is lower than the equilibrium concentration.

To predict the steady-state concentration of a

VOC, the emission rate of the VOC must first be determined with the help of equation 1:

$$C = ES/VN \quad (1)$$

where C is the steady-state concentration (gm^{-3}) of the VOC, E is the emission rate ($\text{gm}^{-2}\text{s}^{-1}$) of the VOC from a material with surface S (m^2) after a specific drying time, V is the volume of the enclosure (m^3) and N is the air exchange rate (s^{-1}). As the product of V and N is the flow F (m^3s^{-1}) circulating through the test chamber, the emission rate of the VOC can be determined experimentally by equation 2:

$$E = CF/S \quad (2)$$

where C , the steady-state concentration of the compound, is measured from the air leaving the test chamber.

For any coating, the emission rate will vary depending on (a) the VOC being considered, (b) the drying time (time since application) and (c) the air exchange rate. Therefore, if the emission rate of a VOC released by a coating is determined after a certain drying period for a particular air exchange rate, equation 1 can be used to predict the steady-state concentration of the VOC in a specific environment (S , V and N). It should be remembered that E is dependent on N : an increase in N results in a corresponding increase in E [16, 17]. For example, if the N used in equation 1 is higher than the experimental N used to determine E , the real steady-state concentration of a VOC in an enclosure will be higher than the concentration predicted by equation 1.

Experimental methods

Equilibrium concentrations and emission rates were determined for acetic acid and TVOC. Acetic acid was measured because it has been found to be released by wood and most coatings and because it is known for its potential to damage museum artifacts—those made of lead, for example. Experiment 1 was designed to determine the acetic acid equilibrium concentration (C_{eAA}) after the coatings had dried for five weeks. Experiment 2 was set up to determine the acetic acid emission rate (E_{AA}) and the TVOC emission rate (E_{TVOC}) from uncoated and coated red oak samples and from the coatings themselves after a five-week drying period. In addition, a limited set of coatings was used for experiment 3 to study the acetic acid and TVOC emission rate decay over a period of six weeks. Table 1 summarizes these experiments. To compare the two emissive material characteristics (C_e and E), samples were prepared with the same dry film weight to sur-

Table 1 Summary of the experiments

Experiment	Measurement	Drying period (weeks)	Samples	No. of replicates	No. of analyses per replicate
1. Equilibrium concentrations	C_{cAA}	5	Uncoated red oak	6	1
	C_{cAA}		Coating on foil	4	1
2. Emission rates	E_{AA} , E_{TVOC}	5	Uncoated red oak	6	2
	E_{AA} , E_{TVOC}		Coated red oak	3	2
	E_{AA}	5	Coating on foil	4	1
3. Emission rates	E_{AA} , E_{TVOC}	0-6	Coating on foil	3	1

face area ratio. Thermal desorption and gas chromatography were used to detect and measure the VOCs.

Sample preparation

Red oak (*Quercus rubra* L.) was chosen as a reference material and substrate for the coatings because it is one of the most acidic wood species [18]. A single 10-year-old red oak panel was acclimatized in a stable environment, then sanded and cut to obtain samples of 10 × 10cm (plane sawn)

and 0.5cm thickness.

Nine unpigmented and 13 white-pigmented commercial coatings were studied. The solids content of coatings was determined by dividing the weight of the film after it had dried for five weeks by its weight when freshly applied on aluminium foil. Unpigmented coatings and pigmented coatings were applied to aluminium foil (15 × 15cm) (one side) or to red oak samples (all sides) to give a dry film weight to surface area ratio of 50 and 100gm⁻², respectively. With the exception of experiment 3, collection of VOCs commenced after five

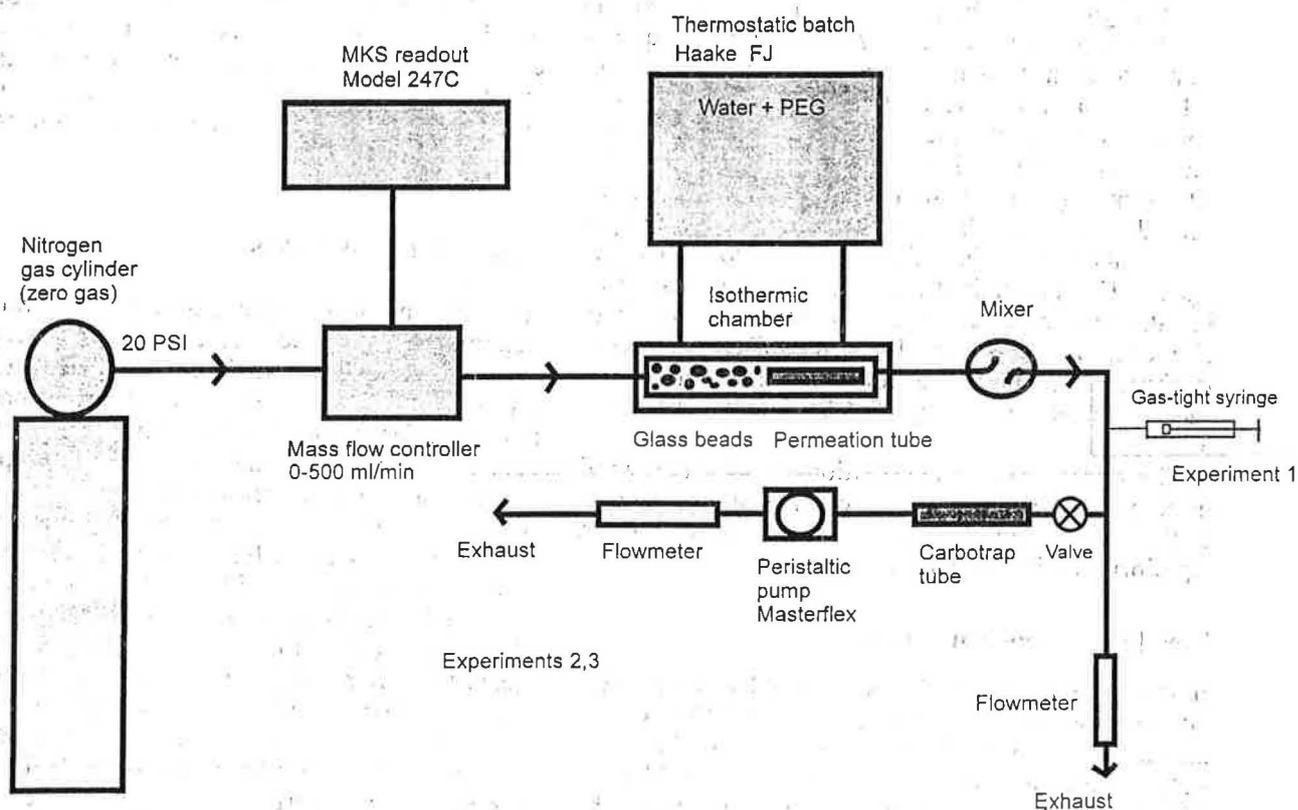


Figure 2 Acetic acid generation system using permeation tubes.

Table 2 Characterization of the white pigmented coating samples

Coatings	Resins*	FFM	Solids content (% w/w)	Experiment 1		Experiment 2	
				Coatings on Al, W/S (gm^{-2})	Coatings on Al, W/S (gm^{-2})	Coatings on red oak, W/S (gm^{-2})	DFT (μm)
Contractor, 917-100, flat, int., Sico	Vinyl acrylic	Co	37 ± 1	99 ± 3	99 ± 2	86 ± 4	28 ± 12
Sicogloss, 266-110, semi-gloss, ext., Sico	Acrylic	Co	50 ± 2	—	94 ± 4	89 ± 10	37 ± 16
Lifemaster2000, 10825, semi-gloss, int., Glidden	Styrene acrylic	Co	47 ± 4	120 ± 3	120 ± 1	112 ± 10	41 ± 14
DTM Acrylic Gloss Coating, B66, high gloss, int./ext., Sherwin-Williams	Acrylic	Co	44 ± 1	111 ± 3	107 ± 3	103 ± 14	37 ± 27
Insul-Aid, Vapour Barrier Primer Sealer, 5116, flat, int., Glidden	Styrene butadiene	Co	45.5 ± 0.5	86 ± 2	104 ± 3	84 ± 14	36 ± 12
Super Urethane Latex Enamel, 261-110, platine, int./ext., Sico	Acrylic urethane	Co	44 ± 2	47 ± 1	94 ± 3	86 ± 2	31 ± 17
Aquaglo, 333-01, semi-gloss, int., Benjamin Moore & Co.	Vinyl acrylic	Co	50 ± 1	86 ± 2	91 ± 2	94 ± 10	42 ± 15
High Performance Epoxy 9101 Activator and 9192 White, Rust-Oleum (Canada) Ltd	Two components; polyamine, polyamide epoxy	Ca	87 ± 9	110 ± 2	110 ± 3	108 ± 10	39 ± 22
Tile-Clad II, B62 W100 and B60 VA7, eggshell, int./ext., Sherwin-Williams	Two components; polyamide epoxy	Ca	62 ± 14	120 ± 3	117 ± 6	121 ± 38	44 ± 32
KEM A&A Epoxy Ester B61, gloss, int./ext., Sherwin-Williams	Single-package epoxy ester	Ox	55.1 ± 0.8	101 ± 4	106 ± 2	92 ± 2	36 ± 10
Epoxy-Flex, 603 320, high gloss, int./ext., Sico	Single-package epoxy ester	Ox	58 ± 4	104 ± 2	117 ± 9	96 ± 3	32 ± 13
Sicovel, 130-110, semi-gloss, int., Sico	Alkyd	Ox	59 ± 2	80 ± 2	87 ± 5	90 ± 19	32 ± 19
Super Sicolux, 154-110, high gloss, int./ext., Sico	Urethane alkyd	Ox	65 ± 4	98 ± 4	107 ± 5	101 ± 3	36 ± 14

FFM = film-forming mechanism, W/S = dry film weight/surface area, DFT = dry film thickness (on wood), Co = coalescence, Ca = catalyzed polymerization, Ox = oxidative polymerization, int. = interior, ext. = exterior

*The nature of the resins is provided by the manufacturers, with the exception of Insul-Aid [15] and Lifemaster2000 [41].

Concentrations of acetic acid emitted from wood coatings

Table 3 Characterization of the unpigmented coating samples

Coatings	Resins*	FFM	Solids content (% w/w)	Experiment 1		Experiment 2	
				Coatings on Al, W/S (gm^{-2})	Coatings on Al, W/S (gm^{-2})	Coatings on red oak, W/S (gm^{-2})	DFT (μm)
Latex Varnish, 166-105, gloss, int., Sico	Acrylic	Co	27 ± 4	79 ± 2	83.7 ± 0.8	70 ± 9	22 ± 8
Crystalex, 195-100, gloss, int., Sico	Acrylic urethane	Co	28 ± 2	70 ± 2	53 ± 6	67 ± 2	24 ± 12
Acryl II, 88, gloss, int., Robar	Acrylic	Co	17.9 ± 0.4	55 ± 1	48 ± 4	42 ± 3	19 ± 8
Acqua Polyur, 2000, gloss, int., Robar	Acrylic urethane	Co	28 ± 2	47 ± 3	82 ± 1	52 ± 3	27 ± 13
Polyur, MC62, semi-gloss, int., Robar	Moisture-cured urethane	MC	34.4 ± 0.5	69 ± 2	66.2 ± 0.9	50 ± 9	19 ± 12
Isothane, 500-0, gloss, int., MF Paints	Moisture-cured urethane	MC	40 ± 2	60 ± 5	72 ± 3	68 ± 3	26 ± 15
Maxithane, 203-090, gloss, int., Sico	Oil-modified urethane	Ox	42 ± 2	49 ± 1	31 ± 3	49 ± 1	21 ± 8
Super Urethane, 68, flat, int., C-I-L	Oil-modified urethane	Ox	44 ± 3	54 ± 2	51 ± 3	46 ± 2	20 ± 11
Orange Shellac, Mohawk Finishing Products	Shellac	SE	23 ± 2	58 ± 1	58.6 ± 0.8	56 ± 5	20 ± 12

FFM = film-forming mechanism, W/S = dry film weight/surface area, DFT = dry film thickness (on wood), Co = coalescence, MC = moisture-cured polymerization, Ox = oxidative polymerization, SE = solvent evaporation, int. = interior, ext. = exterior

*The nature of the resins is provided by the manufacturers.

weeks of drying at $23 \pm 3^\circ C$ and $50 \pm 5\%$ RH in a well-ventilated room. The experiment results have been obtained under one set of relative humidity (RH) conditions pertinent to museum display and storage. Different numerical values for emission rates and equilibrium concentrations would have been obtained in experiments conducted at different relative humidities but the overall trends would not be expected to differ from those reported.

To estimate the dry film thickness of each coated wood, an optical microscope with a fine focus thickness adjustment was used. After the analysis, four small 'windows' were scraped through the coated wood to determine the position of the wood and coating surfaces.

The characteristics of the coatings and coated wood samples used in experiments 1 and 2, includ-

ing solids content, weight and coating thickness, are shown in Table 2 (white-pigmented coatings) and Table 3 (unpigmented coatings).

As the dry film weights per surface area for unpigmented and pigmented coatings are not the same, some caution is necessary when comparing the relative performance of the coatings. However, these dry film weights will be close to those used by painters (e.g., two layers of oil-modified urethane or four layers of shellac).

Calibration of the steady-state acetic acid concentration

To establish a calibration curve for acetic acid vapour, a gas generation system using permeation tubes produced by VICI was used following stan-

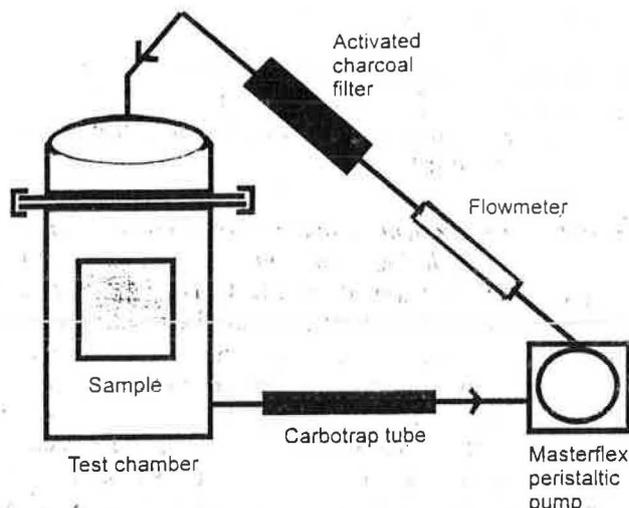


Figure 3 System for collecting VOCs from samples.

standard method ASTM D3609-91 [19] (Figure 2). Permeation tubes were held at constant temperature in a carrier gas stream of nitrogen to generate a specific acetic acid concentration. For the determination of the equilibrium concentration (experiment 1), a 50ml air sample was taken with a gas-tight syringe through the tubing. For the determination of emission rate (experiments 2 and 3), in one exhaust gas stream, a peristaltic pump (Masterflex model 7543-30) forced the air through an absorbent Carbotrap 300 tube at 0.4mls⁻¹ for 19 hours. The Carbotrap 300 tube was designed to trap compounds with at least two carbon atoms.

Collection of VOCs

Experiment 1: Equilibrium acetic acid concentration after a five-week drying period

For the determination of C_{eAA} , samples of coatings on foil were allowed to dry for five weeks, then placed in a 500ml glass vessel with a Teflon/silicone rubber septum for one week. A 50ml air sample from each glass vessel was taken with a gas-tight syringe. Preliminary analysis had shown that the C_{eAA} for red oak and high-emissive coatings was reached in less than two days. In the case of non- or low-emissive coatings on red oak, the C_{eAA} may not have been reached at the time of analysis (after one week in the enclosure).

Experiment 2: Emission rates after a five-week drying period

For the determination of E_{AA} and E_{TVOC} from uncoated red oak, coated red oak and the coatings themselves, a VOC collecting system was designed (Figure 3). Airflow through a 1.4l glass vessel was created by a peristaltic pump at 0.4mls⁻¹. This

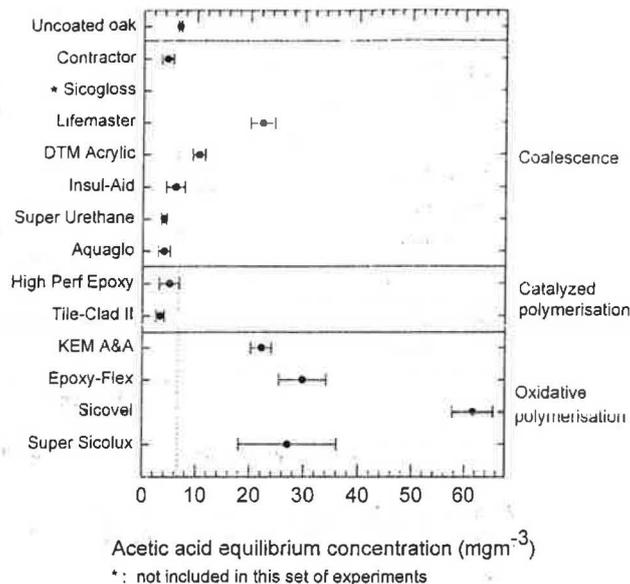


Figure 4 Equilibrium concentrations of acetic acid emitted from pigmented coatings on aluminium foil.

gave one air exchange per hour (i.e., $N = 1h^{-1}$). The peristaltic pump forced the air through the Carbotrap 300 tube for 19 hours. An activated charcoal filter was added between the peristaltic pump and the glass vessel to adsorb any VOCs released by the Norprene rubber tubing (caused by mechanical stress at the head pump rotation on the tubing) before they entered the glass vessel. The tight seal at the junction of the two ground-glass surfaces of the test chamber was established by a cross-linking polyethylene gasket squeezed by two metal clips. Before assembly, glass vessels were heated in an oven for two hours at 150°C to desorb any previously adsorbed compounds. To flush the ambient air in the glass vessel and to minimize adsorption by the glass, glass vessels were acclimatized with the sample inside for three hours before the collection of VOCs commenced.

Experiment 3: Emission rates over the first six weeks

The procedure used to study the emission rate decay of coatings over a six-week period was similar to that for experiment 2, except for the re-use of the sample and the collection period. Before VOCs were collected, glass vessels were acclimatized for three hours with the sample inside. For the initial measurements, which were taken five hours after the preparation of the coating, VOCs were collected for only 15 minutes to avoid saturation of absorbent tubes. When the coatings were dried for one and two weeks, the VOCs were collected for eight and 15 hours, respectively. All the subsequent collections were done for 19 hours.

Concentrations of acetic acid emitted from wood coatings

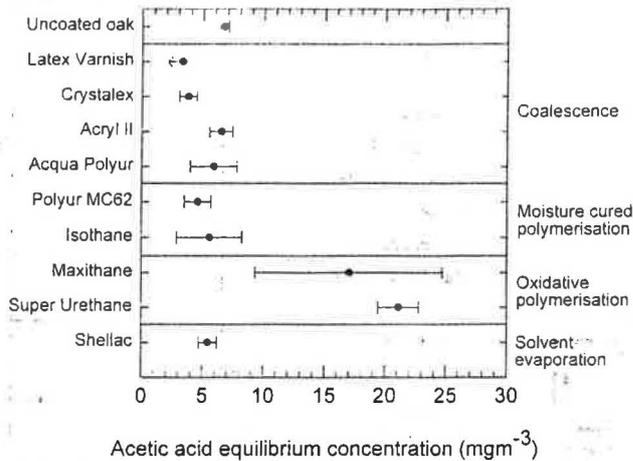


Figure 5 Equilibrium concentrations of acetic acid emitted from unpigmented coatings on aluminium foil.

Detection and measurement of VOCs

Experiment 1: Equilibrium acetic acid concentration after a five-week drying period

VOCs sampled by syringe were injected into the thermal desorption unit (from Dynatherm Analytical Instruments Inc., model 890), then delivered with a helium flow of 0.15mls⁻¹ onto a gas chromatograph (Hewlett Packard model 5890) with a DBWax-30X capillary column. The oven was

programmed to remain at a constant 40°C for two minutes and then to increase to 160°C at a rate of 0.33°Cs⁻¹. A mass spectrometer (Hewlett Packard model 5970) scanned only mass 60me⁻¹ for acetic acid and 94me⁻¹ for phenol (used as an external standard).

Experiments 2 and 3: Emission rates after a five-week drying period and over the first six weeks VOCs trapped by the Carbotrap were desorbed by thermal desorption and then transferred to the gas chromatograph, as described for experiment 1. However, the mass range scanned by the mass spectrometer was 20–320me⁻¹. For the determination of acetic acid, only mass 60me⁻¹ for acetic acid and 94me⁻¹ for phenol were measured in order to avoid interference from other compounds with the same retention time as acetic acid or phenol. The acetic acid standard curve was also used to determine E_{TVOC} (including acetic acid) from the coated wood.

Results

Experiment 1: Equilibrium acetic acid concentration after a five-week drying period

The equilibrium concentrations of acetic acid emitted from pigmented coatings on foil are shown in

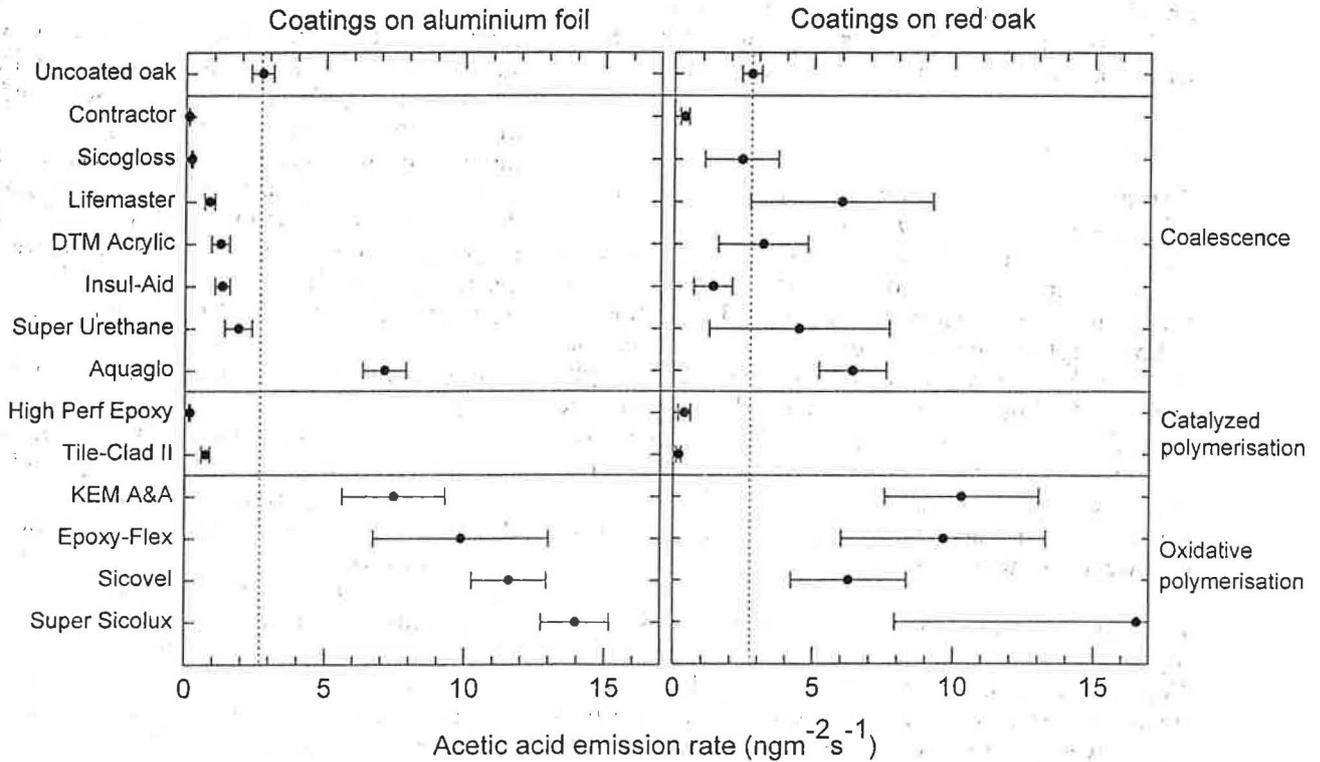


Figure 6 Acetic acid emission rates for pigmented coatings.

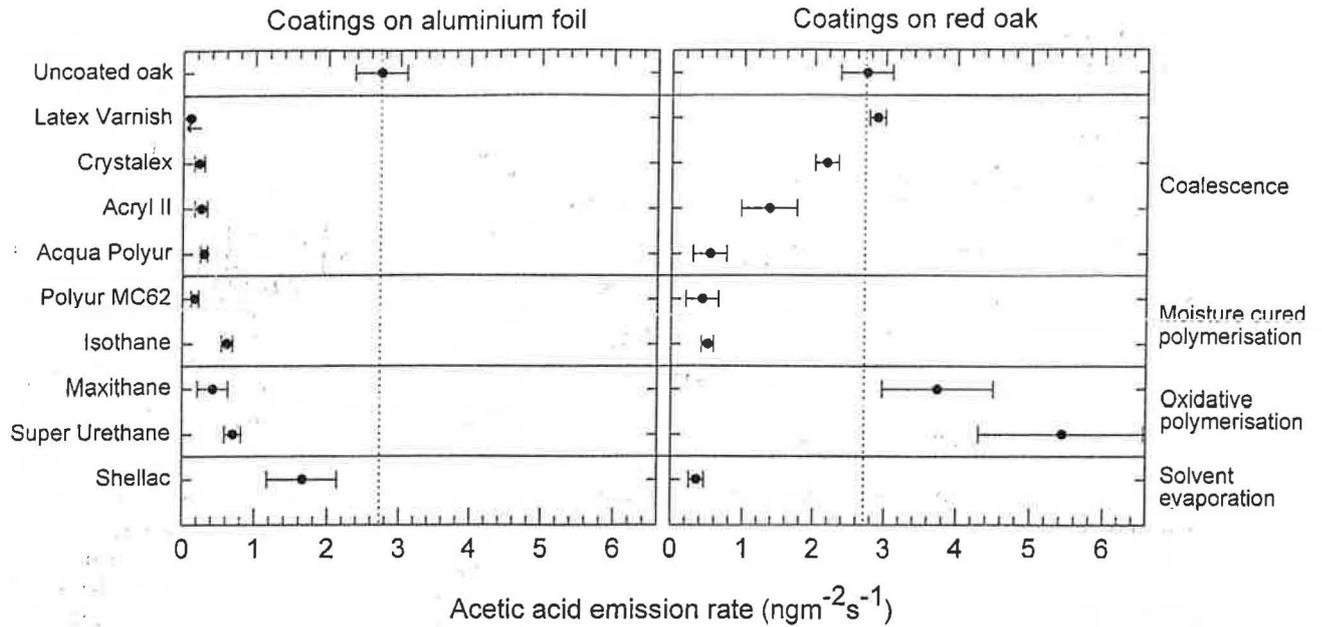


Figure 7 Acetic acid emission rates for unpigmented coatings.

Figure 4. The C_{eAA} ranged from the limit of detection (3.5mgm^{-3}) up to 65.6mgm^{-3} . Oxidative polymerization was the most emissive film-forming mechanism ($17.7\text{--}65.6\text{mgm}^{-3}$). The C_{eAA} for coatings formed by catalyzed polymerization and the majority of coatings formed by coalescence was equal to or lower than that for uncoated red oak (6.7mgm^{-3}).

Unpigmented coatings showed mainly two C_{eAA} ranges (Figure 5): a high range for those formed by oxidative polymerization ($9.4\text{--}24.5\text{mgm}^{-3}$) and a low range (equal to or lower than that for uncoated red oak) for those formed by solvent evaporation, coalescence and moisture-cured polymerization. The C_{eAA} of the Latex Varnish was below the limit of detection.

Experiment 2: Emission rates after a five-week drying period

Acetic acid emissions from uncoated and coated red oak and the coatings themselves

Acetic acid emission rates for pigmented coatings after five weeks of drying are shown in Figure 6. For the coatings on aluminium foil, the E_{AA} from the coatings formed by catalyzed polymerization and most of films formed by coalescence were lower than the E_{AA} from uncoated red oak ($2.7\text{ngm}^{-2}\text{s}^{-1}$). The higher acetic acid emitters ($6\text{--}15\text{ngm}^{-2}\text{s}^{-1}$) were mainly coatings formed by oxidative polymerization. The E_{AA} for the coatings applied to samples of red oak was similar to those for the coatings on foil, except that the rates were slightly higher for

most coatings formed by coalescence. Red oak coated with Sicovel was found to release $6.2\text{ngm}^{-2}\text{s}^{-1}$ of acetic acid. This is lower than the value of $11.5\text{ngm}^{-2}\text{s}^{-1}$ that was obtained for Sicovel applied on aluminium foil, but these values are probably within experimental error.

For unpigmented coatings (Figure 7), the E_{AA} for coatings on foil were all lower than the E_{AA} for uncoated red oak, and the E_{AA} for Latex Varnish

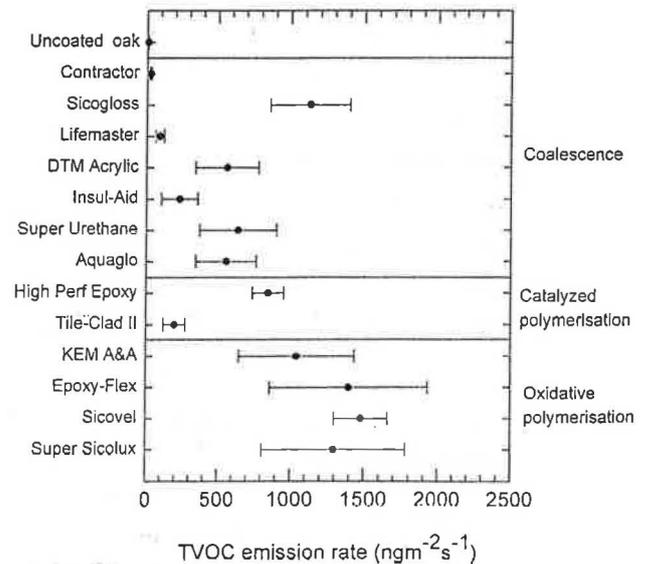


Figure 8 TVOC emission rates for pigmented coatings on red oak.

Concentrations of acetic acid emitted from wood coatings

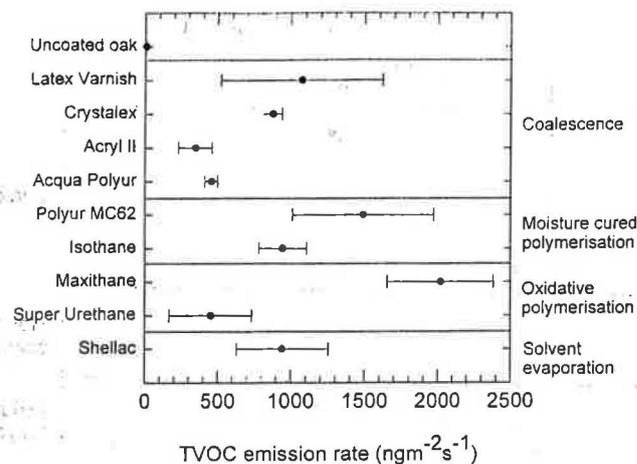


Figure 9 TVOC emission rates for unpigmented coatings on red oak.

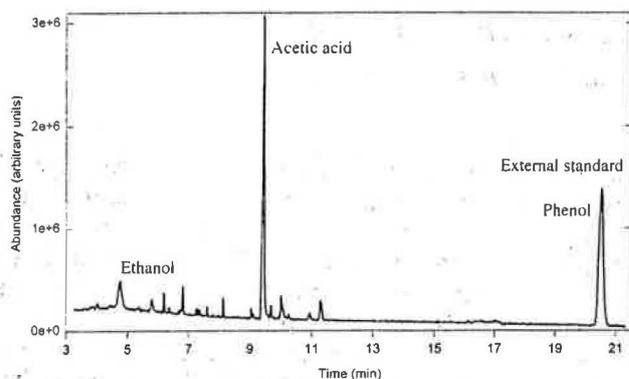


Figure 10 Chromatogram of VOCs emitted from uncoated red oak.

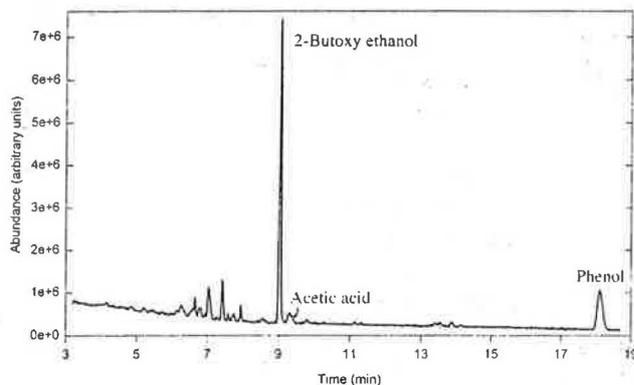


Figure 11 Chromatogram of VOCs emitted from red oak coated with Tile-Clad II.

was lower than the limit of detection ($0.09\text{ngm}^{-2}\text{s}^{-1}$). Similar to the results for the pigmented coatings, E_{AA} was higher from the unpigmented films formed by coalescence when applied

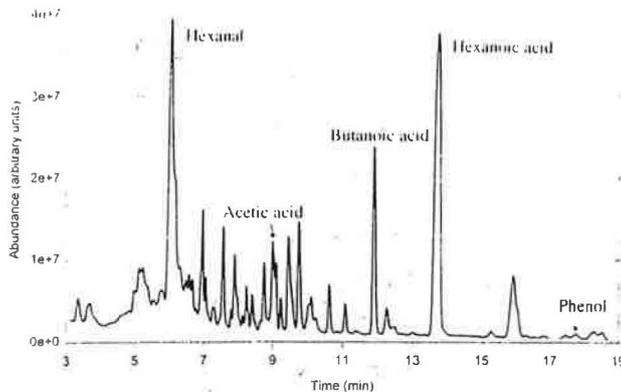


Figure 12 Chromatogram of VOCs emitted from red oak coated with Super Sicolux.

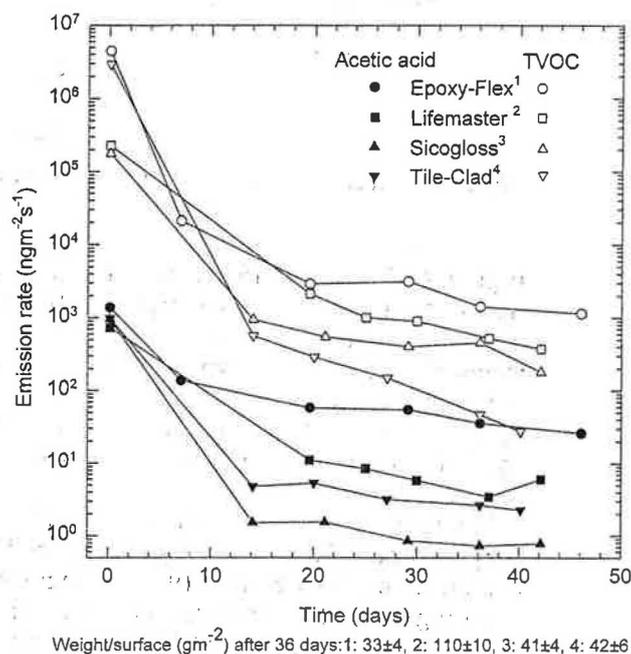
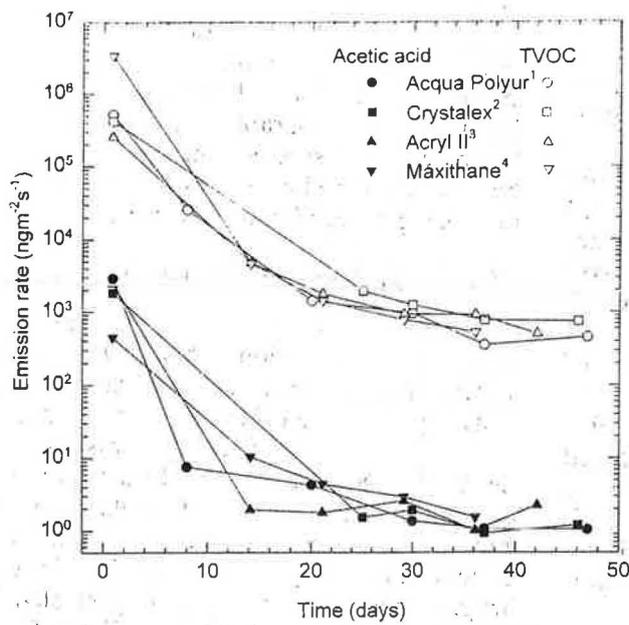


Figure 13 Emission rate decay of some pigmented coatings.

on wood than when applied on aluminium foil. The unpigmented coatings formed by oxidative polymerization also showed a marked increase in E_{AA} when applied to wood. Red oak coated with shellac was found to release only $0.3\text{ngm}^{-2}\text{s}^{-1}$ of acetic acid compared to the value of $1.6\text{ngm}^{-2}\text{s}^{-1}$ when applied on aluminium foil. As for Sicovel, these values are probably within experimental error.

Based on Figures 6 and 7, films formed by solvent evaporation and moisture-cured and catalyzed polymerization, when applied on red oak, were found to reduce the E_{AA} of the red oak by 80–95%. For films formed by coalescence, some films reduced the E_{AA} of the red oak by up to 80%, whereas one of the pigmented films increased the E_{AA} by 140%.



Weight/surface (gm^{-2}) after 36 days: 1: 62 ± 5 , 2: 53 ± 6 , 3: 67 ± 9 , 4: 101 ± 9

Figure 14 Emission rate decay of some unpigmented coatings.

TVOC emissions from coated red oak

Coated red oak was found to have higher E_{TVOC} than uncoated red oak (Figures 8 and 9); only $4.5 \text{ ngm}^{-2} \text{ s}^{-1}$ of TVOC was emitted by red oak, compared with emissions as high as $2500 \text{ ngm}^{-2} \text{ s}^{-1}$ for coatings formed by oxidative polymerization. Only the pigmented films Contractor and Lifemaster2000, formed by coalescence, had E_{TVOC} lower than $100 \text{ ngm}^{-2} \text{ s}^{-1}$. The chromatograms of VOCs emitted from uncoated red oak and from red

oak coated with Tile-Clad II and Super Sicolux show typical emissions from low and high VOC emissive coatings (Figures 10, 11 and 12).

Experiment 3: Emission rates over the first six weeks

The decays in the emission rates of acetic acid and TVOC for eight coatings over a period of six weeks are shown in Figures 13 and 14. The greatest decrease in the VOC emission rate occurs in the early stage of drying. With the exception of E_{TVOC} for Tile-Clad (Figure 13), it was found that the E_{TVOC} and E_{AA} for pigmented coatings levelled off after 20 days. For the four unpigmented coatings studied, E_{TVOC} and E_{AA} levelled off after 30 days (Figure 14). The E_{TVOC} and E_{AA} decay patterns for the unpigmented coatings were similar, with E_{TVOC} being roughly 700 times higher than E_{AA} after 20 days.

The emission rate decay pattern will differ depending on the VOC that is being monitored. For example, it has been reported that formaldehyde (methanal) reaches its lowest emission rate after 20–120 days [20–22], whereas ammonia requires only 1–15 days [21]. Other studies have shown that the lowest emission rates for TVOC are reached between six and 300 days [23]. The extremely long 300-day period was explained by the high level of white spirits used as a solvent in the production of an alkyd binder. However, even a low emission rate may still be considered potentially harmful to objects. Some volatile or semi-volatile organic compounds will remain almost permanently in the dry coating [24].

Table 4 Range of acetic acid concentrations from steady state ($N = 1 \text{ h}^{-1}$) to equilibrium in a 1 m^3 enclosure

Emissive materials	Drying period (weeks)	E_{AA}^* ($\text{ngm}^{-2} \text{ s}^{-1}$) ($N = 1 \text{ h}^{-1}$)	Predicted C_{AA} (mgm^{-3}) ($N = 1 \text{ h}^{-1}$, $S = 5 \text{ m}^2$, $V = 1 \text{ m}^3$)	C_{AA}^\dagger (ngm^{-3})
Red oak		2.6	0.047	6.7
Epoxy-Flex	1	150	2.7	130
	3	60	1.1	52
	5	35	0.63	30
	7	20	0.36	17
Acqua Polyur	1	10	0.18	59
	3	4.5	0.081	27
	5	1.0	0.018	5.9
	7	1.0	0.018	5.9

* E_{AA} of uncoated red oak and coatings are from Figures 6 and 7.

†All C_{AA} of uncoated red oak and coatings after a five-week drying period are from Figures 4 and 5. The C_{AA} of coatings after other drying periods were assumed to be proportional to the E_{AA} of the coatings after those drying periods.

Discussion

Use of emission rates to predict acetic acid concentrations in an enclosure

Table 4 provides examples of acetic acid concentrations for leaky enclosures and for enclosures of optimum airtightness (equilibrium). Predicted steady-state acetic acid concentrations obtained from the relation $C = ES/VN$ (equation 1), are given for three hypothetical enclosures with a volume of 1m^3 , an air exchange rate of 1h^{-1} (which corresponds to a poorly made leaky enclosure) and a surface area of 5m^2 (one side being glass); one of these enclosures has five sides made of red oak, the second has five sides painted with Epoxy-Flex (oxidative polymerization) on an inert substrate and the third has five sides painted with Acqua Polyur (coalescence), also on an inert substrate. In this condition, the rate of condensation of the acid was small, providing barely noticeable error in the value of predicted steady-state concentrations.

Equilibrium acetic acid concentrations for these enclosures have been predicted by taking the value of C_{eAA} at five weeks (from Figures 4 and 5), then calculating the predicted C_{eAA} for other drying periods by assuming that they are proportional to the E_{AA} . According to the calculations in Table 4, the leaky enclosure made of uncoated red oak and the enclosure painted with Acqua Polyur will have low steady-state acetic acid concentrations ($<0.1\text{mgm}^{-3}$) after three weeks of drying. However, with a shorter drying period or a more airtight enclosure, the acetic acid concentration can increase by more than two orders of magnitude.

Acetic acid concentrations above 0.5mgm^{-3} from uncoated or coated wooden cabinets have been shown to cause deterioration of lead, tiles, molluscs and eggshells [25]. Prolonging the drying period of a coating is an effective method of decreasing the VOC concentration in an enclosure, up to the point where the emission rate levels off (approximately 30 days for those coatings studied); additional time beyond this point will have a minimal effect. If the VOC concentration in the enclosure remains unsatisfactory, other palliative methods [26] should be considered, such as increasing the air exchange rate of the display case, using absorbent materials or decreasing the relative humidity. However, each method can create additional problems. For example, increasing the air exchange rate (by fan, open door or holes) lessens the control of external agents of deterioration, such as dust or insects.

Emissions from wood

As shown in Figure 10, acetic acid is the major VOC emitted by uncoated red oak. The acetic acid

is formed by hydrolysis of the hemicellulose acetyl groups. Its content in wood depends mainly on the sampling methods and the nature of the wood species [27, 28]. Ethanol was also identified in the chromatogram of wood emissions. The identity of the other chromatographic peaks remains uncertain. As some wood species emit more acidic material than others, the choice of wood can be a factor in minimizing harmful emissions [18].

Films formed by solvent evaporation

Shellac was the only film studied that was formed by solvent evaporation. Shellac has a low solids content and requires the application of twice as many layers as the other coatings in order to reach a loading of 50gm^{-2} . The E_{TVOC} was quite high, and the main VOC released by shellac was ethanol. In leaky enclosures, 50gm^{-2} of shellac can be considered a good vapour barrier for acetic acid, as it reduces emission by 90% (Figure 7). However, in an airtight enclosure, the C_{eAA} is just slightly lower than that for uncoated red oak (Figure 5).

Films formed by coalescence

Coatings formed by coalescence are easy to work with and have little impact on the environment. However, their effectiveness as vapour barriers and their VOC emissions are difficult to predict.

The presence of acetic acid in films can be explained either by its use in the coating formulation or by degradation processes in the coating (e.g., hydrolysis). During the coating manufacturing process, acetic acid is sometimes added to decrease the pH in order to help dissolve additives such as thickening agents [29].

At lower emission levels, some acetic acid can be formed by hydrolysis of ester-based additives or solvents, such as cellosolve acetate (2-ethoxyethyl ethanoate), used in some emulsion coatings [30]. During long-term storage, a slow hydrolysis of the acetate group of the resin in emulsions (vinyl acetate: homo or copolymer) may occur. This reaction forms the hydrophilic compound poly(vinyl alcohol) and generates acetic acid and aldehydes.

For pigmented films, pigments and extenders (or fillers), depending on their nature, amount and diameter, can reduce the emission of VOCs either by physically blocking it or by adsorption/reaction. The most commonly used extender in coatings is calcium carbonate, an alkaline compound. It can be added in large quantities, up to 50% w/w. Calcium carbonate reacts with organic acids to form carboxylates [31]. Despite the presence of alkali extenders in coating formulations, acidic compounds are not completely neutralized, and both may sometimes coexist [32]. Other extenders, such as mica, do

not react strongly with acids but could slow down their migration.

The Contractor coating is an interesting case in point. It has a high extender content (~50%) (mainly calcium carbonate), but it is also known that some acetic acid is added during its processing as a pH reducer [29]. When the Contractor coating was applied on aluminium foil, the calcium carbonate reduced the E_{AA} to as low as $0.1 \text{ ngm}^{-2}\text{s}^{-1}$. A similar result was obtained when the Contractor coating was applied on red oak ($0.4 \text{ ngm}^{-2}\text{s}^{-1}$).

Films formed by oxidative polymerization

Although coatings formed by oxidative polymerization are commonly available (e.g., alkyd or oil paint), they are not an appropriate choice for most museum purposes. Oxidative polymerization occurs over a long period and generates various VOCs. Formic acid (methanoic acid) is the major oxidative constituent although, during the first few days, peroxides, some aldehydes and carboxylic acids containing up to 10 carbon atoms have also been identified [11, 33, 34]. In the present study, carboxylic acids containing up to six carbon atoms were found to be released by the Epoxy-Flex even after 46 days. The decay of these acids was found to follow the same pattern as acetic acid. Oxidative activities have been reported for coatings formed by oxidation up to 18 months after their application [15].

Pigmented coatings formed by oxidative polymerization on foil had E_{AA} and C_{CAA} higher than those of red oak. However, unpigmented coatings on foil had lower E_{AA} than red oak alone, although their C_{CAA} were higher. Both unpigmented and pigmented coatings on red oak had E_{AA} higher than those of uncoated red oak.

Films formed by catalyzed polymerization

Studied films formed by catalyzed polymerization emitted low amounts of acetic acid and were good barriers. The main disadvantages of coatings formed by this mechanism are their workability, as they are designed to be applied primarily on metal or concrete surfaces, and the difficulty in finding them in local paint stores.

As described for the coatings formed by coalescence, some acetic acid may be formed from the hydrolysis of ester-based additives or solvents such as cellosolve acetate used in some two-part epoxy formulations [11]. Ethyl and butyl acetates have also been found to be emitted by some two-part polyurethane coatings [22]. The two coatings formed by catalyzed polymerization in this study showed a minimal free acetic acid content.

Films formed by moisture-cured polymerization

Coatings in this category performed well, emitting low levels of acetic acid and acting as good barriers. Their main disadvantage is that they are unpleasant to use because of their VOC emissions, which have a strong odour and irritate the eyes. The moisture-cured urethane is characterized by the presence of isocyanate compounds, which react with ambient moisture. The two unpigmented coatings formed by moisture cured polymerization applied on aluminium foil or on red oak showed low E_{AA} ($<1 \text{ ngm}^{-2}\text{s}^{-1}$).

VOCs: museum concerns and regulations

Coatings are generally very high emitters of VOCs, and the interactions between VOCs and objects are not well understood at present. In addition to acetic acid, such museum contaminants as ammonia, formaldehyde (methanal), sulphuric acid and water have also been emitted from different coating formulations in the early stages of drying [21, 22, 30, 35–37].

To follow VOC regulations [38, 39], paint industries tend to use low-density solvents and high solids contents in their coating formulations. Increasing the solids content of a coating formulation normally reduces the E_{TVOC} at the early stages of the film-forming process. According to the literature, this correlation has been observed for freshly applied films formed by catalyzed or oxidative polymerization, but this relationship is not evident for films formed by coalescence [40]. For all coatings (unpigmented and pigmented) after five weeks of drying, no relationship was found between solids content and E_{AA} or E_{TVOC} either within the same film-forming mechanism category or between categories.

Conclusions

The use of solvent-releasing materials, which include most coatings and adhesives in a museum, may cause problems, particularly for small enclosures such as display cases, cabinets, or boxes used for transportation purposes. The risk is even greater for well-sealed enclosures.

If a coating is applied inside a leaky enclosure, care must be taken in its selection:

- coatings formed by oxidative polymerization can release unacceptable levels of acetic acid
- shellac, a film formed by solvent evaporation, emits low levels of acetic acid and shows good ability to reduce emissions when applied on red oak

- coatings formed by moisture-cured and catalyzed polymerization also perform well; however, the use of films formed by these two types of mechanism can be limited owing to their cost, workability and health concerns
- coatings formed by coalescence, despite their popularity, have a wide range of acetic acid emissions, and their performance is difficult to predict owing to the mixture of porous resin, extenders and free acetic acid in the formulations.

In airtight enclosures, the acetic acid equilibrium concentrations generated by coatings formed by oxidative polymerization were much higher than those from red oak alone (6.7mgm^{-3}). Most of the coatings formed by the other types of mechanism generated an equilibrium concentration close to that of red oak.

Consideration should be given to allowing a sufficient drying period (three–four weeks) before sealing a coated enclosure in order to reduce the concentration of VOCs within the enclosure. If the VOC concentration remains a problem after this drying period, the airtightness of the enclosure should be re-evaluated.

The nature of the components of the coatings may partially explain some emission rates and equilibrium concentrations.

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Suppliers

Carbotrap 300, 301: Supelco Canada, 1300 Aimco Blvd, Mississauga, Ontario, Canada L4W 1B2.
Permeation tubes: VICI Metronics, 2991 Corvin Drive, Santa Clara, CA 95051, USA.
Acryl II, 88, Acqua Polyur 2000 and Polyur MC62: Robar Industries Canada Ltée, 520 Blvd Curé Bouvin, Boisbriand, Québec, Canada J7G 2A7.
Aquadlo 333-01: Benjamin Moore & Co., Info Peinture, 77 rue Montclair, Hull, Québec, Canada G8Y 2E8.

Contractor 917-100, Sicogloss 266-110, Super Urethane 261-110, Epoxy-Flex 603-320, Sicovel 130-110, Super Sicolux 154-110, Latex Varnish 166-105, Crystalex 195-100 and Maxithane 203-090: Sico, 2505 rue de la Métropole, Longueuil, Québec, Canada J4G 1E5.
DTM Acrylic Gloss Coating B66, Tile-Clad II B62 W100 and B60 VA7 and KEM A&A Epoxy Ester B61: The Sherwin-Williams Company, 170 Brunel Road, Mississauga, Ontario, Canada L4Z 1T5.
High Performance Epoxy 9101 Activator and 9192 White: Rust-Oleum (Canada) Ltd, 590 Supertest Road, Downsview, Ontario, Canada M3J 2M5.
Isothane 500-0: MF Paints, 1605 Blvd Dagenais Ouest, Ste-Rose, Québec, Canada H7L 9Z7.
Lifemaster2000 10825 and Insul-Aid 5116: Glidden, 2247 Gladwin Crescent, Ottawa, Ontario, Canada K1B 4K9.
Orange Shellac: Mohawk Finishing Products, 9290 rue Le Prado, St-Léonard, Québec, Canada H1P 3B4.
Super Urethane 68: C-I-L, 8200 Keele Street, Concord, Ontario, Canada L4K 2A5.

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Résumé—Vingt-deux revêtements commerciaux ont été choisis en fonction du mécanisme de formation du film pour étudier la concentration à l'équilibre de phase des composés organiques volatils (COV) et leur taux d'émission en équilibre dynamique. Les concentrations d'acide acétique et des COV totaux sont mesurées grâce à une unité de désorption thermique couplée à un chromatographe en phase gazeuse. Presque tous les revêtements libèrent de l'acide acétique, en différentes proportions. Les revêtements formés en polymérisation par oxydation génèrent les plus hauts niveaux d'acide acétique à l'équilibre de phase et en équilibre dynamique. Les concentrations d'acide acétique en équilibre de phase des revêtements formés par les autres mécanismes étudiés sont similaires à celles du chêne rouge, une essence acide. Dans une situation d'équilibre dynamique, la plupart des revêtements appliqués sur une feuille d'aluminium ou sur un échantillon de chêne rouge ont des taux d'émissions d'acide acétique inférieurs à ceux du chêne rouge seul, à l'exception des revêtements pigmentés formés par coalescence appliqués sur du chêne rouge. Le domaine de concentrations d'acide acétique en équilibre de phase et en taux d'émission des films formés par coalescence est étendu à cause de la présence de résines poreuses, de matières de charge et d'acide acétique libre dans la composition de ces revêtements. Il est conseillé d'allouer une période de séchage suffisante (3-4 semaines) avant d'utiliser des enceintes peintes, de manière à réduire les concentrations de COV à l'intérieur des enceintes.

