

Influence Of The Substrates On Water-based Paints Emissions

Fabio Abbà^{1*}, Mikaela Decio², Tiziano Cerulli² and Roberto Leoni²

¹ Vinavil S.p.A. R & D Laboratory, Via Toce, 7, 28844 Villadossola, Italy

**f.abba@vinavil.it*

² Mapei S.p.A. R & D Central Laboratory, Via Cafiero, 22, 20158 Milan, Italy

SUMMARY

Volatile Organic Compounds (VOC) can be evaluated either as in-can amount in the products or as emissions released by the products as a function of time. The European Directive 2004/42/EC defines VOC every organic compound with a boiling point up to 250°C. Different methods are nowadays available to determine the VOC in many building products. Evaluations of VOC in the product (in-can VOC) can be performed by calculation from the original formulation, gravimetric methods (ISO 11890-1: 2007), gas chromatography (ISO 11890-2: 2006); VOC emissions as a function of time released by the product can be determined by means of emission chambers (ISO 16000-6: 2004).

The aim of this study is to compare different methods, both in-can VOC and emissions, to measure VOC in three water based paints with different formulation (without or with coalescing agents with different boiling points) complying with 2004/42/EC.

IMPLICATIONS

Paints were analysed following ISO 11890-2 in order to evaluate the in-can VOC content and then analysed according to ISO 16000-6, for determination of VOC in indoor air using test emission chambers. The influence of substrates on the total VOC (TVOC) release has been considered and paints have been applied both on a glass plate chosen as non adsorbent substrate according to ISO 16000 and on a sound-deadening panel as an adsorbent surface. Data from traditional emission chambers have also been compared with the ones obtained by micro-chambers (μ -CTE) technique with various implications about the results obtained.

KEYWORDS

Water Based paints, in-can VOC, emission chambers, micro chambers.

INTRODUCTION

Different methods are available to determine the Volatile Organic Compounds (VOC) in many building products. VOC evaluations in a product (the so called in-can VOC) can be performed by calculation from the original formulation, gravimetric methods [1] and gas chromatography [2]; VOC emissions can be determined by means of emission chambers [3] as a time function released by the product. The aim of this study is to compare distinct methods, in-can VOC and emissions, to measure VOC in different water based paints.

To better understand the total VOC amount (TVOC) two different substrate a glass plate (non adsorbent) according to ISO 16000 has been chosen and a sound-deadening panel (adsorbent).

METHODS

a) IN-CAN VOC methods

Methods for VOC content measurement need to be flexible enough to cope with any definition of VOC and VOC content.

There are mainly three different used methods to determine in-can VOC content:

- Difference Method (ISO 11890-1- ASTM D3960)

Some features must be determined before expressing VOC such as weight percentage of non-volatile matter (ASTM D2369, ISO 3251), water content (ASTM D4017, ISO 760) etc...

They are used for high VOC content (ISO 11890-1 - weight percent > 15%.)

- Gas-chromatographic methods

1) ISO 11890-2 - measurement of VOC Contents between 0.1 and 15 wt%.

Based on a split-vent liquid injection Gas Chromatography it allows identification and quantification of all volatile components summing those falling within the relevant definition of VOC. This method is reported in the European Directive 2004/42/CE.

After sample preparation, VOCs are separated by a gas-chromatographic technique, then compounds are identified and quantified from peak areas using a suitable internal standard.

A suitable organic solvent, at least 99 % by mass, should be used for diluting the sample. If VOC is defined according to the European Directive 2004/42/CE - maximum boiling point 250 °C - a marker compound of known purity and a boiling point within ± 3 °C of the defined maximum boiling point shall be used (in this ISO standard diethyl adipate with a boiling point of 251 °C, should be used as a marker compound).

2) A head-space gas chromatographic - total exhaustion technique is also applied in the determination of very low in-can VOC content (ISO 17895) ranging between 0.01 and 0.1 wt%.

b) Emission methods

Emission test chambers have been used for years in our analytical laboratory, in order to evaluate the VOC content emitted by building products and adhesives used for flooring installations. Nowadays our analytical lab is equipped with twelve emission chambers and six micro-chambers used for a preliminary screening of samples. Micro-chambers (μ -CTE) cannot be used for the evaluation of VOC according to ISO 16000 and GEV testing method, since they don't comply with a right loading factor, nor for Relative Humidity (RH).

In our experience, μ -CTE are useful to predict a sample behaviour in traditional emission chambers.

The emission chambers, made of stainless steel, have a volume of 100 l, controlled relative humidity and temperature ($T= 23 \pm 1^\circ\text{C}$; $\text{RH}= 50 \pm 5\%$), and loading factor $0.45 \text{ m}^2/\text{m}^3$, as requested by applied criteria. The chambers are fluxed with dry nitrogen (in this text we refer to this gas as "air"), with a flow rate of 0.5 h^{-1} , which allows a complete change of the air in the chamber every two hours. The sample is mixed uniformly, weighed and applied on a glass non adsorbent surface; the test specimen is transferred into the chamber immediately after preparation.

According to the GEV (Gemeinschaft Emissionskontrollierte Verlegenwerkstoffe e.V) testing method, air sampling for testing should start 72 hours after adhesive application. In our experiment we have collected air samples at 72 hours and 672 hours after specimen preparation. At the outlet of test chamber, exhaust air is passed through a sample tube filled with a suitable adsorbent material (Tenax TA®) Tenax tubes are then desorbed by a thermo-desorber; volatile organic compounds are separated by gas-chromatography, identified by MS detector and quantified by FID detector. A second specimen has been prepared by applying the paint on a sound-deadening panel and analysed with the same method.

RESULTS

Three water based paints have been prepared with and without coalescing agents:

Paint A: paint without any coalescing agent;

Paint B: paint with a coalescing agent with a boiling point lower than 250°C;

Paint C: paint with a coalescing agent with a boiling point higher than 250°C.

In can VOC content has been determined using the method above described.

Next table will sum up the quantitative results on the three samples, expressed in g/L.

Table 1. IN-CAN VOC values

Sample	VOC g/L
Sample A	< 1
Sample B	8,8
Sample C	< 1

According to ISO 11890-2 all the three samples comply with the European Directive 2004/42/CE and can be considered as “low-VOC” paints. From the obtained values paint A and C are equivalent.

Micro chambers (μ -CTE)

The three paints have been applied on an aluminium plate and evaluated in μ -CTE at a temperature of 40°C and the air has been sampled after 18 and 24 hours. Table 2 shows results, enhancing that paint A has no emission, while paints B and C show a similar behaviour (but paint C with a higher value), mainly due to the coalescing agents.

Table 2. μ -CTE VOC values

<i>Time h</i>	<i>$\mu\text{g}/\text{m}^3$ aluminium</i>		
	<i>Paint A</i>	<i>Paint B</i>	<i>Paint C</i>
18 h	-	553.8	935.4
24 h	-	300.3	387.2

The samples have been applied on a sound deadening panel to detect possible substrate’s influence also in μ -CTE. Even in this case paint A does not reveal any emission while paint B and C has a similar behaviour (Table 3).

Table 3. μ -CTE VOC values

<i>Time h</i>	<i>$\mu\text{g}/\text{m}^3$ sound-deadening panel</i>		
	<i>Paint A</i>	<i>Paint B</i>	<i>Paint C</i>
18 h	-	255.2	305.4
24 h	-	146.5	143.1

Traditional emission chambers

The same paints have been analysed according to ISO 16000 in order to evaluate their real influence on indoor air quality. In the first part of the experiment, a sample film thickness of about 100 μm has been applied on a glass plate, as established by the normative. Results are then normalized for a weight of 200g/m². The concentration of coalescing agents in the first hours is very high and the peaks might have been saturated.

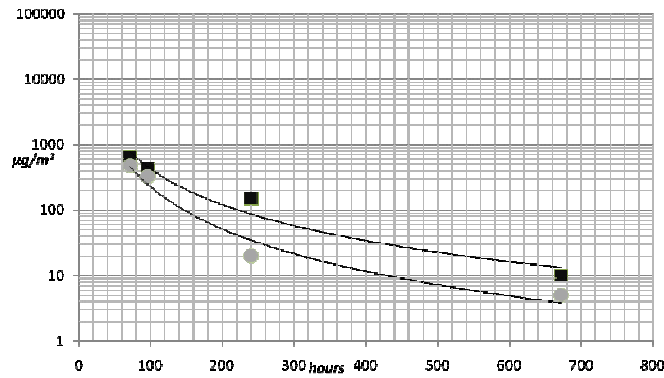


Figure 1. Paint A- panel emissions ■ glass ○ sound deadening panel

Table 4. Paint A- panel emission compounds

<i>Time (hours)</i>	<i>µg/m³ glass</i>	<i>µg/m³ s-d</i>
72 h	640	475
96 h	435	324
240 h	150	20
672 h	10	5

Paint A shows very low emissions from the first 72 hours, due to the glycols in the formulations. After 672 hours (28 days), the detected emissions are so low that if the product applied were an adhesive, according to GEV criteria, it would be considered as EC1 plus (very low VOC emission product). The application of paint A on the sound deadening panel shows that the VOC content detected can be absorbed by the substrate.

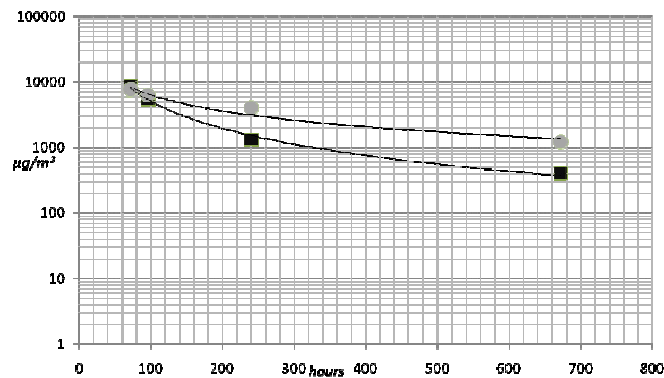


Figure 2. Paint B- panel emissions ■ glass ○ sound deadening panel

Table 5. Paint B- panel emission compounds

<i>Time (hours)</i>	<i>µg/m³ glass</i>	<i>µg/m³ s-d</i>
72 h	8435	7622
96 h	5405	6210
240 h	1321	3986
672 h	405	1204

Paint B emissions are pretty higher than the first formulation on both substrates, due to the presence of the coalescing agent. 28 days after product application, emissions slightly decrease so we hypothesize that coalescing agent will be released for several weeks.

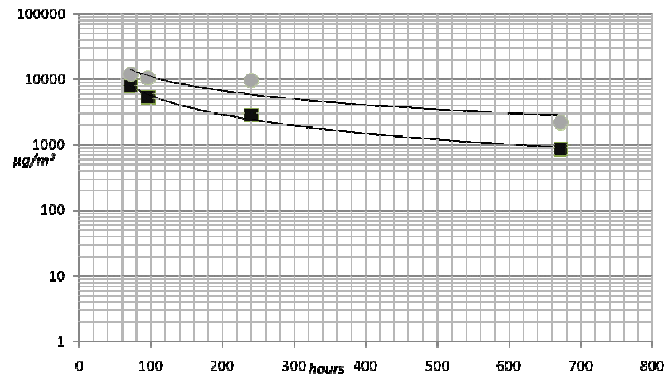


Figure 3. Paint C- panel emissions ■ glass ○ sound deadening panel

Table 6: Paint C- glass panel emission compounds

<i>Time (hours)</i>	<i>µg/m³ glass</i>	<i>µg/m³ s-d</i>
72 h	7854	11853
96 h	5350	10548
240 h	2843	9571
672 h	850	2200

Paint C has been formulated adding a high boiling point coalescing agent and the emissions released by the product are very high after the first 72 hours, due to it. The emission value after 28 days has been strongly influenced by the presence of the coalescing agent which hardly decrease in time.

DISCUSSION

The report below sums up all the results found out by applying the various methods:

Table 7. summary (TVOC 28 days)

<i>Samples</i>	<i>IN-CAN VOC (g/l)</i>	<i>TVOC µ-CTE µg/m³</i>	<i>TVOC µg/m³ glass</i>	<i>TVOC µg/m³ s-d panel</i>
Paint A	< 1	-	10	5
Paint B	8.8	271	405	1204
Paint C	< 1	341	850	2200

Paint A and C are considered equivalent from IN-CAN VOC determination while paint B has the highest VOC content.

Only total VOCs content value obtained on aluminium plate after 24 hours has been reported for µ-CTE since the absorbing substrate seems to level the situation.

Emission results in the traditional chambers on the three paints are quite different compared with IN-CAN VOC and strongly amplified in the case of the absorbing substrate use (sound-deadening panel).

The strong influence of coalescing agents presence in the paints seems not to be detected by the in-can method but it is very relevant considering indoor air quality.

Pre-screening with µ-CTE on aluminium plate reveals a different behaviour between paint B or C and paint A.

On the other hand the analysis on traditional chambers highlights that:

- due to the absence of additives, paint A has always very low emissions from the two substrates both in µ-CTE and traditional emission chambers;

- paint B contains a VOC coalescing agent (bp < 250°C) contributing to a higher VOC in-can value (but inside the limit of European directive): the TVOC emission at 672 h is entirely due to this additive;

- paint C has a low VOC value according with IN-CAN method because contains a coalescing agent not considered VOC (bp > 250°C): but this high boiling point this component is so difficult to be released that the paint reveals a TVOC value at 672 h higher than paint B.

Considering the different substrate used in this experiment, it is shown that the release of volatile and semi-volatile compounds is very slow. After 3 days application's paint the detected emissions are comparable between the two substrates; after 28 days the observed emissions are quite higher on the absorbing substrate than on glass.

CONCLUSIONS

The emission test chamber method is applied, according to GEV voluntary scheme only on adhesives, self levellers, primers and sealants.

This scheme prescribes application, for instance, of an adhesive on a non adsorbent glass plate which enhances all the possible emissions coming from the product, even if an adhesive is usually applied on a mortar layer and covered with tiles, wood etc. reducing total VOC emissions.

On the other hand paints are usually applied on a wall (gypsum, sound-deadening panels etc..) and this fact can directly influence indoor air quality.

Nowadays in Europe the only recognized method to evaluate VOC content in paints is the in-can VOC method; in US "LEED for school" [5] rating system, a test emission chambers method is requested for the evaluation of paints and coatings for to contribution of one point in credit IEQ 4.2.

This work illustrates that an in-can VOC is not sufficient to properly describe indoor air quality, but the complementary emission method is necessary to depict the whole scenario.

The pre-screening with micro chambers is helpful to predict a certain paints behaviour, but the emission with traditional chambers is essential to describe the phenomena in indoor environment.

Since a coalescing agent is a long time releasing substance, a new project is in progress to deeply evaluate this parameter as well as the influence of some other layers such as gypsum, gypsum + primer etc.. with micro chambers and traditional chambers.

ACKNOWLEDGEMENT

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