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## THE DISINFESTATION OF HISTORICAL MONUMENTS: GAS SUBSTITUTES FOR METHYL BROMIDE

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### ABSTRACT

All areas involved by heritage protection are concerned by infestation problems. Historical buildings and their collections show more significant problems due to the difficulty in intervening in situ and the fact that, quite often, artefacts cannot be conveyed or disassembled. Environment of such areas is favourable to the development of insects and moulds. Attacks to materials, especially wood, require disinfection by chemical treatments. Until recently, methyl bromide was the fumigant of choice because it has no adverse effects. Because of its phase out under terms of the Montreal Protocol due to its ozone - depleting properties it has been necessary to find alternatives. Candidate alternatives are sulfur dioxide (Vikane®), phosphine, dimethyl disulfide (DMDS) - use for soil fumigation as nematicide and fungicide - and cyanogen ('ethanedinitrile'), general disinfectant. These alternatives if used for furniture disinfection within the framework of historical monuments may have effects on decorative elements. Also, wall paintings may include pigments and reactive gildings (gold containing decoration). It is of the highest importance to study, on selected samples, the effect of the fumigation treatments on these units of our cultural heritage. Consequently, an experiment with all these gases was carried out to define the various important physicochemical interactions with artefacts. In order to observe the effects of such gases with time on optical properties of pigments on historical artefacts, samples were artificially aged, then compared with reference samples.

**Keywords:** fumigation treatments, gildings, infestation, metal artefacts.

### INTRODUCTION

Conservation of historical monuments and artifacts in them need pest control measures. When preventative measures fail, it is necessary to use curative methods, and, among them, fumigation. Until recently, methyl bromide was used for this purpose but it was banned under the Montreal Protocol in 2005 in developed countries. It may be replaced by sulfur dioxide (SF) registered in France in 2006, in the heritage field. It has already been subject of

publications related to its application to cultural heritage (Su, 1999). Other fumigants considered in this study are phosphine (PH<sub>3</sub>), already well known, mainly for wood objects, and two other compounds, dimethyl disulphide (DMDS) and cyanogens ('ethanedinitrile', (EDN), which have valuable properties as insecticides but also as fungicides. In order to observe the effects of such gases with time, samples were artificially aged, then compared with reference samples kept in an air conditioned room.

## MATERIALS AND METHODS

### Fumigations

Fumigations were carried out in gastight stainless steel fumigation chambers of 1 m<sup>3</sup> for PH<sub>3</sub>, DMDS and SF, and in a rigid PVC 200 L chamber for EDN. These chambers were held in an air conditioned room, maintained at a temperature of 15°C ±1°C and r.h. 50 % ± 5 %. The mode of gas introduction was different, according to their properties.

Phosphine was generated from aluminum phosphide pellets to give 2 g m<sup>-3</sup> of phosphine for an exposure time of 7 days. Ten pellets giving by hydrolysis 0.2g PH<sub>3</sub> each were put in a dish.

DMDS was placed as a liquid in a petri dish. A fan was used to increase vaporization and to mix the gas in the chamber. The dosage was 60 g m<sup>-3</sup> and exposure time 24h.

SF was injected as a gas from a small cylinder containing 1.5 kg of liquid and the quantity was measured by weight placing this cylinder on a scale. A fan was run to mix the gas in the chamber. The dosage was 150 g m<sup>-3</sup> and exposure time 24h.

C<sub>2</sub>N<sub>2</sub> was injected as a gas at a dosage of 200g m<sup>-3</sup>, exposure time 24h. The gas was introduced with a 2 L Hamilton gastight syringe with the displaced air allowed to escape at the opposite side.

The ct-product (CTP) obtained was calculated to give a good measure of the activity of the introduced fumigant, except for phosphine where the only rule was that the concentration was maintained at over 200 ppm anytime (Ducom, 1999). Concentrations were measured at three levels in the chambers with an electrochemical cell for PH<sub>3</sub> (model MX2100, Oldham), and by thermoconductivity for DMDS, SF and EDN, (Fumiscope). The gas concentrations presented in table 3 show average concentrations, but the values throughout the chamber were very close.

### Gilded Samples

To analyze the fumigation effects on the heritage materials, test pieces were produced according to ancient techniques of gilding (gold leaf application) on panel paintings and on stone, with both supports commonly found in the heritage area.

On panel paintings, nine types of gilding have been applied, following the data sourced from ancient texts (Perrault, 1992). The basic preparation is common to all samples. The underlayer was composed of several calcium carbonate layers to which a 10 % skin glue had been added. This is known as distemper gilding here. Various types of gildings were applied to this preparation (Table 1).

On stone (limestone), seven types of gildings have been tested. The stratigraphic structure of the gilded samples is shown in Table 2.

Table 1. Gildings on wood panels, used in the studies

B1	Distemper gilding (gold) on Armenia bowl (skin glue)
B2	Distemper gilding (gold) on Armenia bowl (skin glue) + rabbit skin glue varnish
B3	Distemper gilding (gold) on yellow pigment layer (skin glue)
B4	Powder gilding (gold) on yellow pigment layer
B5	Distemper gilding (silver) on Armenia bowl (egg)
B6	Distemper gilding (silver) on Armenia bowl (egg) - dammar varnish
B7	Distemper gilding (brass) on Armenia bowl (egg)
B8	Mixtion gilding (brass) on yellow pigment layer
B9	Powder gilding (bronzine) on yellow ochre pigment layer

Table 2. Gildings on stone, used in the studies

P1	Mixtion gilding (tin) on red ochre layer
P2	Mixtion gilding (tin) on blue azurite layer
P3	Mixtion gilding (tin) on red cinnabar layer
P4	Distemper gilding (gold) on Armenia bowl (skin glue)
P5	Distemper gilding (gold) on Armenia bowl (egg)
P6	Mixtion gilding (tin + gold) on red ochre pigment layer
P7	Mixtion gilding (gold) on red ochre layer

### Artificial ageing

Artificial ageing seeks to simulate the degradation processes of the materials. The hygrothermal ageing protocol developed previously (Aze, 2005) was used. This ageing (V1) reproduces 8-hour cycles that follow the temperature and relative humidity variations recorded in the Aix-en-Provence cathedral during a year. Samples were submitted to 90 8-hour cycles (= 1 month) each cycle consisting in a succession of 4 climate phases for a duration of 90 minutes each, with linear transitions of 30 minutes: (a) High humidity phase (r.h. = 85 %, T = 18°C); (b) Low temperature phase (r.h. = 0 %, T = -10°C); (c) Dry heat phase (r.h. = 25 %, T = 40°C); (d) Wet heat phase r.h. = 60 %, T = 30°C).

Light ageing (V2) is cumulative, unlike the hygrothermal ageing (Feller, 1994). Samples were submitted to UVB (313 nm) for 400 hours at constant temperature, close to 45°C. The equipment (QUV-Panel, Q-LAB) supplied UVB centered around 313 nm. The spectral irradiance was  $0.71 \text{ W m}^{-2} \text{ nm}^{-1}$  for a standard distance to the tubes of 4.5 cm.

## Methods

Sample preparation (stratigraphic sections): some samples have been embedded in a resin and observed by optical microscopy to examine the alterations due to gases, on the metallic coat and on the preparation coat (underlayer). Samples and their cross-sections are examined and photographed using a Leitz polarizing microscope connected to a digital camera.

A colorimetric survey of the metal surface of the sample has been performed to see the chromatic variations before and after treatment and ageing. The system used is a HunterLab portable equipment, type Miniscan XE Plus 4000S, operating under standard light D65 with an observation angle of 10° allowing spectra acquisition in the 400-700 nm spectral field with a resolution of 10 nm. The analyzed surface was a 6mm diameter disc. Thirty observations were made for each sample, before and after treatment. The average results have been used for the calculation of the colour differences DE\* (Dupont and Steen, 2006).

Some of the materials have been analyzed using a JEOL scanning electron microscope (SEM-EDS) JSM 6460LV (low vacuum) coupled to an EDSX (Oxford INCA 300) energy dispersion X-ray detector.

## RESULTS

### Evolution of gas concentrations during the exposure times

Table 3 shows the evolution of gas concentrations in each chamber. As usual, sorption is high with EDN, but very small with SF. DMDS was vaporized very slowly, 6 hours to give the maximum concentration. The hydrolysis of phosphine was slow, probably because the r.h was low (50%) when the chamber was closed. The rate of evolution of gas was similar to those obtained in good commercial fumigations.

Table 3. Evolution of gas concentrations in each chamber for initial dosages of 200 g m<sup>-3</sup> for EDN, 150 g m<sup>-3</sup> for SF, 60 g m<sup>-3</sup> for DMDS and 2 g m<sup>-3</sup> (1400 ppm) for PH<sub>3</sub>

EDN		SF		DMDS		PH <sub>3</sub>	
Exposure Time (h)	Concentration (g m <sup>-3</sup> )	Exposure Time (h)	Concentration (g m <sup>-3</sup> )	Exposure Time (h)	Concentration (g m <sup>-3</sup> )	Exposure Time (h)	Concentration (ppm)
0	0	0	0	0	0	6	380
1	193.5	1	123.5	2	31.2	24	1033
3	165	5	122	3	45.5	27	1081
6	147	8	123.5	5	56	29	1105
22	94.5	24	120.5	8	48.75	48	1159
24	91.5			24	42.9	72	1108.5
						150	895.5
						168	850
<b>CTP (g h m<sup>-3</sup>)</b>	<b>3041</b>		<b>2873</b>		<b>1061</b>		-

### Gilded panel paintings

Visually, nearly no chromatic variation has been noticed in literature (Koestler et al., 1993). The colorimetric results « refine » these impressions. Some small decreases in brightness and a yellowing have been observed. Variations in DE\* lower than 5 are perfectly acceptable and

are typically reported as insignificant. Generally speaking, on the chromatic point of view, artificial ageing had only a small effect on the gold and silver foils. On the other hand, copper foils were darker.

DMDS and sulfur dioxide gave satisfactory results on the whole samples. Concerning B1, B5 and B7 samples processed by sulfur dioxide, sulphur and chlorine, concentrations higher than those of the reference samples (untreated) were found on a red gesso area revealed by a tear on the metal leaf. These same deposits have been noticed on the rabbit skin glue which covers the gold leaf of sample B2. Studies performed by Getty Conservation Institute (Baker et al., 1990; Derrick et al. 1990) already showed this fact. It seems that they are due to gas impurities. For this reason, purification of the matter before fumigation was required. So, a filter consisting of small marble stones was installed between the sulfur dioxide cylinder and the treatment chamber.

In the case of DMDS, higher sulphur concentrations have also been noted by SEM-EDS on the surface of the red gesso. As with sulfur dioxide, sulphur does not seem to induce alterations to the red gesso. Sulphur was also found on the dammar varnish on the surface of sample B6. No significant variations were found on the dammar varnish spectrum processed with DMDS versus the spectrum of the unprocessed sample, but under the influence of the UV ageing. The sample covered with dammar varnish and processed with DMDS became highly yellowed ( $Db^* = 12.9$ ).

Concerning  $C_2N_2$ , very poor results were found on samples B1, B3 and on copper alloys (B7, B8 and B9).

Hydrogen phosphide gave satisfactory results on samples B1 to B6. But the effects were disastrous on the copper alloys of samples B7, B8 and B9. Such results could be anticipated based on a previous study (Bertholon, 1993). These samples as well as samples B4 showing a too small gilded surface have been intentionally discarded from the colorimetric investigation. Some surface depositions have been featured by SEM-EDS. Concerning hydrogen phosphide, high phosphorus concentrations were found on samples B7, B8 and B9 (copper alloys). Phosphorus traces are also found on the skin glue of sample B2 as well as on the silver leaf. Because of its action on copper,  $C_2N_2$  should be prohibited from use for historical monument treatment. The three other treatments gave satisfactory results as a whole, except hydrogen phosphide on copper alloys.

### **Gilding on stone**

Colour evaluations were performed on the reference samples, on samples treated by the three gases and then on the aged samples (Fig. 1).

The effect of the treatments on the luminance is not statistically significant. All the evaluations are based on the colour difference  $DE^*$ . For the four treatments, a slight blackening or tarnishing of the surfaces of the tin leaf gildings (P1, P2 and P3) was noted.

$C_2N_2$  treatment has the highest effect on the colour of the gildings. The cyanogen ( $C_2N_2$ ) treated and non-aged gildings (T4V0) showed a blackening of the metal surface of gold leaves (PM5, PM6 and PM7) and a marked yellowing of P4 (as if an opaque varnish coat had been superficially applied).  $C_2N_2$  has a small effect on tin (P1, P2 and P3), just a small «lightening» of the metal leaf.

### **DMDS is the treatment having the lowest effects.**

An assessment of the effects of some fumigants on pigments and metals shown that sulfur dioxide induces visible modifications of the zinc and lead appearance (Kigawa et al., 1999). As to pigments, tests performed on painting samples made of proteinaceous lacquer coating

containing linseed oil plus a mixture of white lead and oil and at last a pigment coat (cobalt blue, Prussian blue, yellow ochre,...) showed that sulfuryl fluoride affected most of the samples in terms of change in colour and brightness (Koestler et al., 1993).

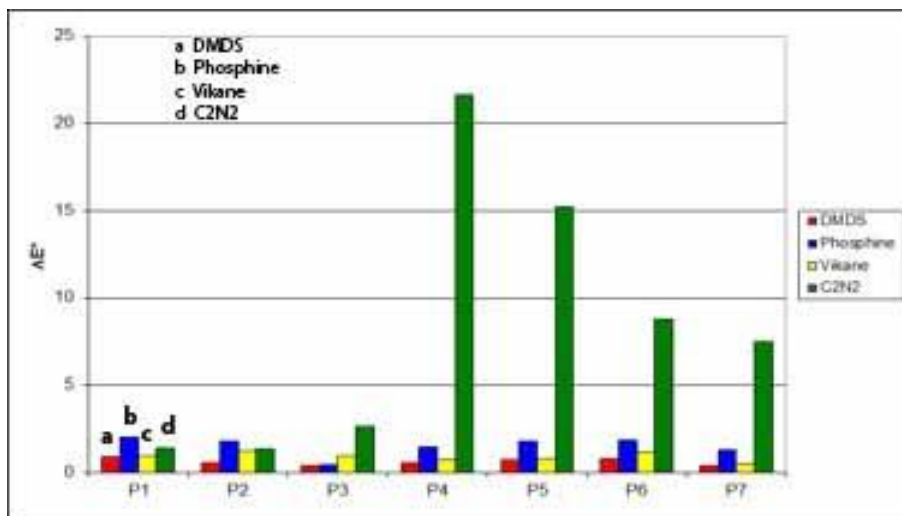


Fig. 1- Colour difference (DE\*) of the gildings with regard to the references (controls).

An alteration of azurite with phosphine was visible on tin gildings on azurite (P2). When the copper based pigment was used, it became black (Fig. 1). This reaction was expected as azurite is a copper based pigment  $\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$  and it has been shown previously that phosphine had a high corrosion effect on copper and copper alloys (Bertholon, 1993).

#### Effect of ageing on treated gildings

Figs. 2 and 3 show the effects of the hygrothermal (V1) and light (V2) ageing on the treated samples. Hygrothermal ageing appeared to be the most harmful to the conservation of gildings (Fig. 2), especially on samples treated following distemper gilding. The highest effect was noticed with DMDS (DE\* values from 4 to 8) and  $\text{C}_2\text{N}_2$  treated gildings (DE\* values > to 15).

Concerning  $\text{C}_2\text{N}_2$ , on P2, the oil containing binder yellowed and it was noticed that the blue azurite pigment turned to green. V1 results in small modifications for tin gildings treated by  $\text{C}_2\text{N}_2$ . For zwischgold gildings, a deep yellowing of the P4 and of the P5 gold was noticed as well as a network of surface small cracks. The highest alteration pertinent to all ageings relates to gold gildings with a proteinaceous binder: high metal shrinkage and « deflaking » of the metal leaf carrying the red ochre coloured layer and a « Dry » appearance with, sometimes, a nearly complete disappearance of the gold. Concerning gold gilding, a high yellowing of the metal surface followed by dulling was noted. For both distemper gilding samples no data has been recorded, the metal leaf having suffered a lot: gold leaf « deflaking » and shrinkage, and material loss.

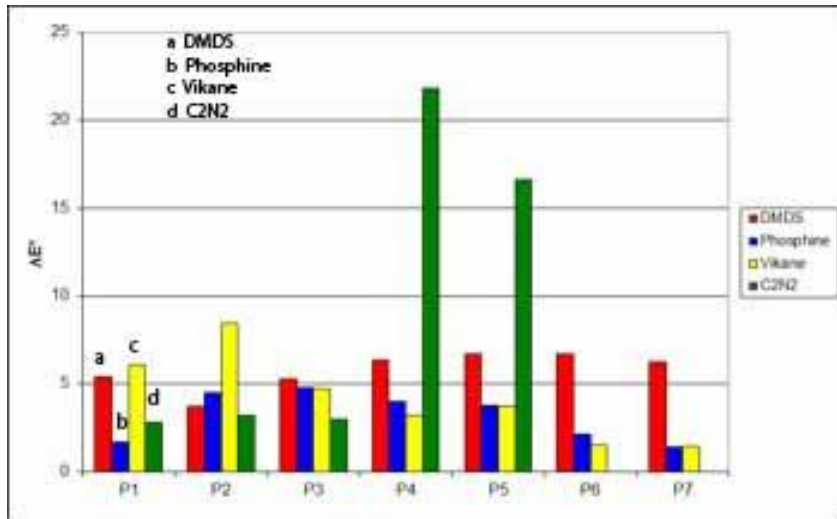


Fig. 2- Colour difference (DE\*) with regard to the aged references (hygrothermal ageing V1).

Except for C<sub>2</sub>N<sub>2</sub>, UV ageing does not seem to have produced such effects on gilding (Fig. 3), but gold gilding intensive dulling and yellowing was observed. No significant colour deviation after UV ageing was noted.

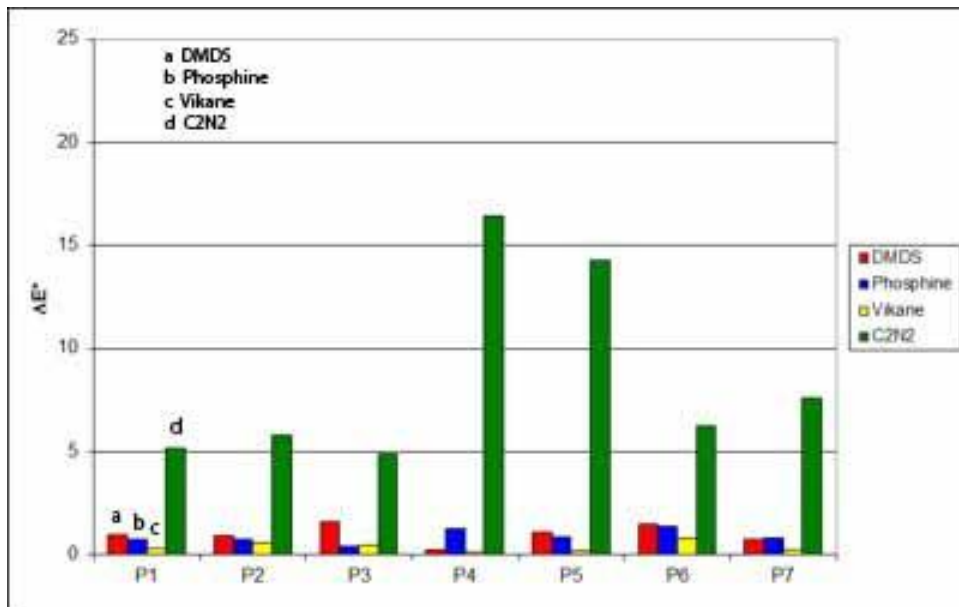


Fig. 3- Colour difference (DE\*) with regard to aged references (light ageing V2).

For C<sub>2</sub>N<sub>2</sub> treated samples, a dulling of the metal surfaces (loss of the bright metal aspect, for P1, P5 and P7) and sometimes a yellowing of gold which becomes more «pasty», more orange (P2, P4) has been noticed. Also there was metal delamination and the metal

formed a network of small cracks with P4 and P5. These results and observations show that C<sub>2</sub>N<sub>2</sub> is not a suitable disinfestation method for this type of materials.

## CONCLUSIONS

The objective of this study was to be able to select the best fumigant as a fumigant for historical monuments and artefacts as an alternative of methyl bromide. However, each gas showed advantages and limits and the best choice should be a compromise considering all the parameters, whatever the processing, cost and alterations of the materials.

Phosphine does not give satisfactory results. Indeed, it is totally discarded due to its irreversible effects on copper alloys, in spite of its easy application. On painted plasters, this gas induces the highest colour alterations after treatment, especially on gold gildings. It should not be recommended for the disinfestation of heritage premises in the presence of metal artefacts with silver, copper (or alloy containing copper), tin or lead.

Study performed on gilded wood panels shows that DMDS, which is not registered in France today, could give satisfactory results, except its very persistent garlic smell and dammar varnish yellowing under light. Should these effects be confirmed, they, undoubtedly, would result in the withdrawal of this gas for this utilization.

Results and observations show that using C<sub>2</sub>N<sub>2</sub> as disinfection agent seems to be compromised and not suitable to this type of materials.

DMDS and EDN have less corrosive effects than phosphine. However, they lead to changes on all metals tested, higher for copper and lead, and result in instability of the compounds during ageing. They should not be recommended.

Sulfuryl fluoride gives satisfactory results, as the impurities in the technical grade can be eliminated thanks to the installation of a filter. Studies performed by the Getty Conservation Institute were favourable as far as the use of SF on cultural heritage artefacts is concerned. Among others, several churches have been treated in Germany and no noticeable effect has been reported. Recently, in France, the first fumigation applied to a historic monument (Hauteluce church) has been performed in 2007. Despite of its very high cost and that the required active substance has to be at least double that for methyl bromide for the same efficiency, sulfuryl fluoride (Vikane) is the most suitable substitute gas for methyl bromide.

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## APPENDIX

### **Nomenclature of gases and samples:**

Gas: No treatment (T0), DMDS (T1), hydrogen phosphide (T2), sulphuryl fluoride (T3), C<sub>2</sub>N<sub>2</sub> (T4).

Ageing: No ageing (V0), hygrothermal ageing (V1), light ageing (V2).

The effects of gases with time can be analyzed from the comparison of artificially aged samples and compared with the reference samples (T0V0): no treatment, no ageing. Indeed, the effects of gases with time can be analyzed from the comparison of artificially aged



samples and compared with the reference samples submitted to the same ageing (T0V1): no treatment and hygrothermal ageing and (T0V2): no treatment and light ageing.

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