Investigations on pollutants gaseous in museum environments

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The Museum of Art of São Paulo Assis Chateaubriand - MASP was founded in 1947, but only in 1968 was installed on the modern building of concrete and glass at Avenida Paulista. Shortly after its last revitalization in 2000 (Fig. 34), there were detected grey points and spots (Fig. 35) in bronze sculptures that were in exhibition in the museum exhibition hall. The research began with the raising of all new materials inserted in this space after renovation. For many years now British care and study the various types of pollutants within and outside of museums. In 1973, the British Museum in London developed a relatively simple and inexpensive system, which allows analysing any and all new material introduced in its galleries. Developed by Andrew Oddy, the *Oddy Test* has as principle to analyse gases possible to be emitted by diverse material introduce in its galleries. The test is run on copper, lead and silver plates sealed in a glass container along with the material wishing to be analysed and puts the kit to high temperature and humidity. Each of these metals will be responsible to detect different components that might eventually harm the conservation of works of art.

I. Strategy

With the revitalization project, many new materials were introduced in the museum, including the air conditioning system in closed circuit, which was completely replaced. The museum has several exhibition areas and a deposit, which are located at different levels and with different materials in their internal structure. A first survey found that the area that should be considered was the gallery where the bronzes that had shown the greyish stains were. At the time, all bronzes that were on the exhibition gallery were taken and an inquiry of recent changes at the exhibition space was made. All new materials introduced were listed, searched and analysed.

II. First Analysis

Based on the system of *Oddy Test,* the first tests were made in the laboratory and in galleries of the museum with the probable materials. For laboratory tests were separated samples of *MDF*[1] *(Medium Density Fiberboard),* material used in partitions of the exhibition space, and of the rubber floor. The tests with plates of copper and lead with samples of *MDF* and floor were assembled in glass bottles sealed, keeping or not a beaker of water in its interior and submitting the set to a temperature of about 50˚C.

The tests in the gallery were prepared directly on the rubber floor. A small beaker was put on the ground and supported on it was the copper plate, so it did not remain in direct contact with the floor. The larger beaker was placed with the opening downward, closing the atmosphere surrounding the smaller beaker on the floor. With help of melted microcrystalline wax, the large beaker was sealed on the ground, providing exposure to the metal plates to a specific microclimate. This latest test was performed on the room temperature of the gallery (about 22˚C).

Still for the gallery analysis, there were prepared two prototypes of wood, one painted with white lead in linseed oil and the second with white lead in Arabic gum. These two samples were placed on the gallery and visually analysed. Any colour change in the samples could suggest that the paintings were undergoing changes caused by the internal atmosphere of the gallery. For these samples, no changes were made visible.

Besides the results of the tests mentioned above, samples, of all materials introduced into the environment of the gallery after the revitalization of the museum, were also sent to be analysed on IPT (Institute of Technological Researches). Samples of the following material were separated, examined by scanning electron microscopy (Fig. 36) and analysed by energy dispersive scan (EDS):

- new rubber floor of the gallery: floor consisting of tire reclaimed rubber, styrene-butadiene rubber, agalmatolite, carbon black, sulphur, MBTS and MBT[2];

- old rubber floor of the gallery (similar to the current one);

- MDF (Medium Density Fiberboard): used in constructing partitions of the exhibition walls and the bases on which the sculptures are exposed;

- adhesive mortar used for bonding the floor during the remodel of the space;

- sealing compound used on the glasses surrounding the museum galleries.

The air conditioning system was also analysed. In this case, the analysis was made by X-ray diffraction. The obtained samples were the following:

- sample residue stuck on the first filter through which outside air passes as being caught by the museum air conditioning system;

1 MDF is a derivative of wood, manufactured by agglutination of wood fibbers with synthetic resins and other additives.

2 MBTS and MBT are trademarks of organic accelerators, which have as function assist in the process of rubber vulcanizing.

- 20cm x 20cm piece of the filter through which air from the gallery passes before going back to the same room.

In addition to diagnosing potential pollutants in the environment, it was essential correlate those with the grey stains on the surface of the bronzes. For this purpose, microscopic samples were taken from one of the bronze sculptures diagnosed with the problem, and the samples were analysed by X-ray diffraction. The following samples were removed:

- two samples of the bronze used in the making of the sculpture (scraped superficially in the inner area of the support base);

- two samples of the patina on the surface of the sculpture (obtained by superficially scrapping, under a inoculate magnifying glass);

- two samples of the patina covered by the grey stain (obtained by superficially scrapping, under a binocular magnifying glass).

Based on researches made with suppliers, it was found that the *MDF* used as partitions and bases in the exhibition galleries has from 9.1 to 40 mg of formaldehyde in its composition, while the *MDF* destined to exportation has less than 9.1 mg of formaldehyde.

III. Results of the first analysis

From pre-history, of all existent materials, copper and its alloys are the materials most known to man. Its great importance is primarily related to the ability to associate good corrosion resistance in various environments, excellent workability and high electrical and thermal conductivity, besides good mechanical properties.

When the copper and its alloys are exposed to clean atmospheres, at room temperature, forms on the surface a thin layer of cuprous oxide (Cu2O) with a small amount of cupric oxide (CuO). The increase of thickness of this layer is limited by the diffusion of copper ions. As the oxide layer becomes thicker and more compact, the diffusion of copper ions becomes more difficult, the growth rate of oxide decreases and the thickness of the oxide layer tends asymptotically to reach a value close to 5.10-3 µm. After two days of exposure, this condition is reached and after this period, the growth tendency of oxides decreases significantly. The layer can be quite thin and invisible, enough however to ensure the copper and its alloys excellent corrosion resistance.

When the copper and its alloys are exposed to atmospheres with small quantities of sulphidric gas, the layer formed will consists of oxides and copper sulphide, being that the amount of sulphur contained in the oxide layer is proportional to the active sulphur in the atmosphere. The presence of copper sulphide disrupts the oxide layer, introducing a larger amount of crystal defects, which in turn favours the occurrence of diffusion processes through it. As a result, the oxide layer grows at higher rates than those found in clean atmospheres. In those conditions, the thickness of this layer will be greater than 5.10-3 μm, and will determine the appearance of interference colours.

If the atmosphere is contaminated with sulphur dioxide, such as urban and industrial ones, with the exposure time, changes on the dark layer that will gradually assume a greenish colour appears. This layer, called patina, is highly protective and ensures to copper an excellent corrosion resistance, and usually, the time for its formation is very long and depends on climatic conditions and on the content of sulphur dioxide in the atmosphere, it may take five to thirty years. In addition to sulphur dioxide, other pollutants can also contribute to the formation of the patina; it can be mentioned carbon dioxide and chlorides.

However, when copper and its alloys are exposed to atmospheres significantly contaminated with sulphur compounds, the layer of corrosion products will form on a high speed and therefore not optimally, presenting porous and a high thickness.

Of the results on the analyses by energy dispersive scan (EDS) performed on samples scraped from work in bronze (patina with grey stain and patina without blemish), the most important was the detection of contamination with the elements sulphur (S) and chlorine (Cl), the detection of the elements most likely related to the particulate material in suspension in the atmosphere of exhibition area (silicon (Si), aluminium (Al), calcium (Ca), potassium (K), titanium (Ti), magnesium (Mg)) and the detection in high level, only on the patina without blemish, of the element carbon, which is due, very probably, to the presence of an organic layer, possibly wax. The results of the analyses by energy dispersive scan (EDS) performed on copper plates submitted to tested sets with a sample of the new rubber flooring and tested in the gallery, showed contamination by sulphur.

The literature is unanimous to state that the process of vulcanization of a rubber continues for a certain period of time, even after the end of the manufacturing process. However, there are authors who claim that while the vulcanization process has not terminated there is release of sulphur by-products, and others state that, for this release would be necessary exposure of the rubber to a temperature of at least 150 ˚ C.

The detection of sulphur in high concentrations in copper plates submitted to sets tested with a sample of new rubber floor and tested in the gallery shows that the first line of authors is correct: if the vulcanization process has not terminated, there is release of sulphur by-products. Therefor, the source of the contamination with sulphur was detected: the rubber floor installed in the revitalization of the museum.

Because from the materials removed and installed in revitalization, the element Cl was only detected in the rubber floor removed during the remodel, its origin in the patinas with and without grey spot may be related, for example, to a volatilization of cleaners products previously used, a handling of the work in an inappropriate manner (without gloves) or exposure of the work, at some time in its existence, to a marine atmosphere.

With the identification of the origin of contaminations by chlorine and sulphur, we started to aim at the identification of compounds that would be responsible for the greyish colouring of stains under study. For this purpose, samples of air conditioning filters were analysed by X-ray diffraction. The results showed that the two compounds detected in the area of the patina covered by greyish stains were also detected in the air captured from outside the Museum and the air that circulates in the gallery, such as: silicon oxide (alpha quartz), and carbon (graphite), being those essential constituents of solid matter suspended in the atmosphere (particulate matter). According to literature, the alpha-quartz (silicon oxide) often shows a colourless or white colour, may eventually present itself coloured due to the presence of impurities, and carbon (graphite) features colour between black and grey steel.

From the results shown we have that the rubber floor installed in the gallery released by-products of the vulcanization process containing sulphur and allowed the formation of a layer of corrosion products on the surface of the bronze sculptures that were exhibited on an irregular manner. This, in turn, when exposed to deposition of particulate material allowed the “trapping” of compounds such as carbon (graphite) that gave a characteristic coloration to those areas (greyish stains).

Areas that presented a patina (natural corrosion layer) intact, i.e. without the presence of greyish stains, were, most likely, protected by layer of wax once applied on the works in bronze. That was confirmed by the presence of carbon at high levels in these regions.

It should be noted that the air conditioning system working in closed circuit allowed the air inside the gallery to present a concentration of sulphur compounds that increased with time.

Similar analyses were made later on several other occasions and found that the process of vulcanizing rubber tends to finish.

IV. Analyses in glass cases

Aiming to confer if the acrylic cases, commonly used in the exhibition of sculptures and objects, would form a protective barrier against environmental pollutants, we proceeded to a new analysis. To perform this test it was designed an acrylic cases with *MDF* base, as is usually done in the museum. Inside the dome was glued silica gel so to maintain a low relative humidity (between 40% and 50%) and copper, silver and lead[3] plates, which were supported on an acrylic holder (Fig. 37). Similarly, metal plates were also placed on the outside of the window but inside the museum gallery. Plates were kept in place and monitored for three months. Samples were analysed by energy dispersive scan (EDS) with the aid of a scanning electron microscope[4].

3 Due to lead and sulphur present elements values very close to the peak of identifying energy, verifying the existence of sulphur in a sample of lead is impossible to be performed using the methodology adopted in this work (analysis by dispersal energy).

4 Brand Jeol, model JSM 6300.

Analysing the results, it was found the presence of the sulphur element on the surface of the plates of silver and copper exposed in both conditions (inside and outside the window). Based on the results mentioned, it is clear that the acrylic cases can maintain protection in relation to the relative humidity, but does not protect against pollutants gaseous.

V. Conclusions

The installation of a new rubber floor in the gallery exposed the works in bronze to an atmosphere contaminated by sulphur compounds. The air-conditioning system, working in a closed circuit, allowed the air inside the gallery to present a concentration of sulphur compounds increasing with time. Exposure of works made of bronze to atmospheres highly contaminated by these compounds led to the formation of a corrosion products layer in a non-protective manner, i.e., presenting porous and a high thickness.

The air-conditioning system in a museum has function and importance beyond the control of temperature and relative humidity. If there is no filtration of solid particles and gaseous elements, even if the external air filtration is efficient, small internal contaminants may take unwanted dimensions. The "clean" airflow within the collection environment is considered fundamental to good conservation. The frequently analysis with the help of silver and copper plates in exhibition spaces can avoid many problems.

Bases with acrylic dome can and should be used in museums, but only for the purpose of physical protection, meaning, to maintain a stable relative humidity, different from external humidity, and for protection of solid particles. However, it is not recommended for protection against gaseous elements.

All and any new materials introduced into environments that have works of art should be tested. If not in laboratory, at least be submitted to *Oddy Test* at a first moment.

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