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FRACTAL ANALYSIS ON CHEMICAL DEGRADATION OF NATURAL RESINS PROTECTOR FILM

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Abstract

This is a study on the fractal analysis regarding the chemical degradation of three types of protector films in air polluted with SO_2. Fractal analysis is a method used to study surfaces properties of protector film. The films composed of natural resins (shellac, colophony and dammar) and ethanol are exposed on atmosphere with SO_2.

Keywords: fractal analysis, protector film, shellac, colophony, dammar

1. Introduction

In preserving art objects, one of the most important rule is to use protector materials, named varnishes, less exposed to degradation.

From the chemical point of view, varnishes are film materials made of resins or a mixture of resins dissolved in a solvent or a mixture of solvents. Resins contain terpenes, acids, alcohols, resin esters and other secondary compounds. Linked to the length of the molecule chain, they have different density and are inert to the activity of physico-chemical agents.

Resins are materials insoluble in water, but they totally dissolve or are partly soluble in oils, alcohols, turpentine essence, etc. The following properties vary a lot with the type of resin: durability, aspect, hardness, solubility, density, smell, brightness, colour and colour stability.

From the hardness point of view the resins used in the artistic field are: tough resins, giving the so-called fat varnishes, and semi–tough or smooth resins giving soft varnishes. Even though they are easier to apply, the soft resins are very sensitive to heat, give more friable varnishes and they are subjected to biological attacks. From their composition, resins can be naturals or synthetics.

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The films made of natural resins have a special protecting role to the outer destructive agents and in order to amplify the brightness of the painting layer. In their absence the painting layer rapidly decay under the action of moist, heat, dust, UV radiation, fungi etc.

Generally speaking, the protecting films for objects of art need to carry out the following conditions [1]:

- to be colourless or transparent;
- to be applied in a thin, uniform and continuous layer;
- to not affect colours;
- to be soluble in organic solvents;
- to have physical and chemical stability;
- to be reversible;
- to have a good covering capacity etc.

Among the most used natural resins for varnishes we mention dammar, mastic, colophony and shellac [2].

Colophony is a residue from the distillation of conifer resins, especially from pines, after removing the oil and the turpentine essence. In its composition there are mainly resin acids and a small quantity of resins and resinols. It is a transparent material or yellowish, breakable and sticky, which is dissolved in almost all volatile solvents and in oils. The protecting films of colophony have the tendency of darkening and cracking and a reduced resistance to water.

Shellac is a resin of animal origin, the secretion of a kind of louse. The colour of the resin can be white, orange, or brown depending on purity. Shellac is soluble in ethylic alcohol, borax, ammonium, formic acid and insoluble in turpentine essence. The films of shellac are tough, resistant and flexible, but they have the tendency to darken and are sensitive to water.

Dammar is any of a variety of hard varnish resins obtained from coniferous trees characteristic of Southeast and East Asia, especially the amboyna pine. It is a highly aromatic product.

The resistance of a varnish is determined by the characteristics of the environment but depend on the composing materials as well. Among the environment elements which affect a protecting film we mention: moist, light, temperature, dust and atmosphere noxa agents.

Previous researches [3] showed that a polluting gaseous atmosphere have negative effects both to the resisting properties and flexibility, and to the aesthetic properties of the protecting film. Hence, there appear micro-cracks, cracks, striations and vesications.

Fractal geometry offers a new approach to describe the structure of different irregular objects. The fractal theory has been increasingly applied in the field of materials science and engineering. Models of fractal lines and surfaces have been generated to describe the microstructural features of materials. Special interest is placed upon a description of the fracture surface based on fractal geometry, in order to understand the crack path in materials. Several papers have demonstrated the relationship between the fractal dimension of a fracture surface and the values of roughness and fracture toughness [4-6].

One of the most noxious agents of chemical decay for many types of materials constitutive of art object is sulphur dioxide.

2. Experimental

It was studied the influence of the noxious gaseous atmosphere on natural varnishes, from the solving of shellac and colophony resins in ethylic alcohol and their setting on polypropylene foils by drying at the ambient temperature. The dimension of the samples was 2x2 cm.

Among the environment elements which influence the protecting painting films there was chosen the sulphur dioxide, known for its high noxious effects. There was created a hermetical enclosure rich in sulphur dioxide obtained 'in situ'. The films were exposed to the activity of the decaying agent in concentration of 0.1 mg/L SO_2.

The obtained protector films were analysed using SEM Tesla BS 800.

3. Results and discussion

In Figures 1-3 there is observed the SO_2 decaying action on the surface of shellac, colophony and dammar films, proved by numerous cracks and fine cracks.

In order to prove the modifications produced by SO_2 on the varnish film, the fractal analysis was performed. HarFA specialized software was applied to obtain fractal dimension for every samples [7]. In HarFA is used a modification of traditional Box Counting Method. By this modification one obtains three fractal dimensions, which characterise the properties of black plane DB, black-white border of black object DBW (and this information is the most interesting) and the properties of white background DW. The fractal dimension is the slope of the straight line 'Black&White' [5].

The photos from Figures 1-3 were prepared with the Adobe Photoshop in order to obtain the black and white images and to use the HarFA soft.

The fractal dimension for the shellac samples is given in Figure 4. The fractal dimensions for the samples from Figures 1-3 are presented in Table 1.

Fractal analysis is a method that could be used to study surface properties of biomaterials [8]. Feder [9] suggested that the fractal dimension depends on porosity and there is a relationship between the amounts of water withheld by a material and its fractal dimension.

Our results show that the fractal dimension increases for shellac and dammar samples and decreases for the colophony when these varnish firms are polluted with SO_2. Therefore shellac and dammar are more resistant than the other films under of SO_2 action due their chemical structure which confers them resistance to the sulphur attack.

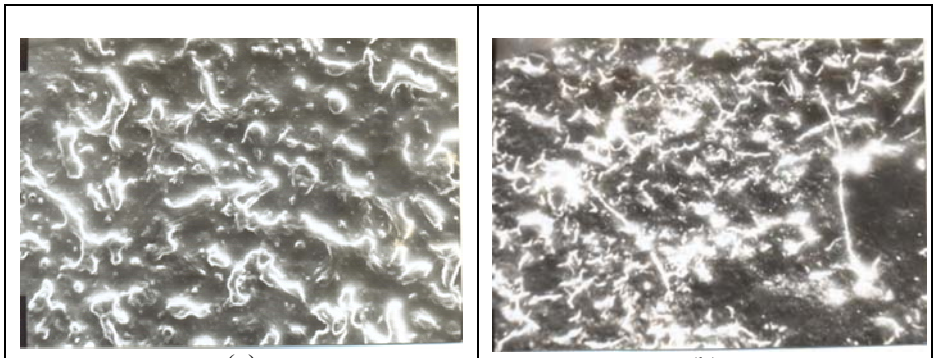

Figure 1. (a) Varnish film based on shellac - reference (x180); (b) the effect of chemical pollution with SO_2 on the shellac varnish (x180).

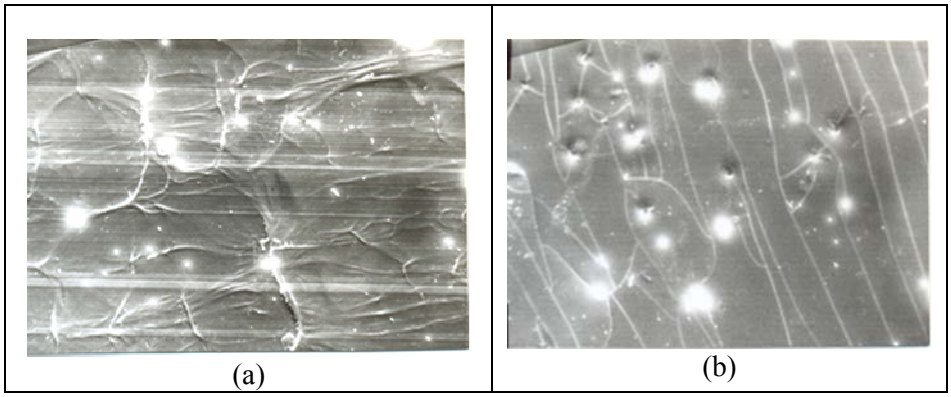

Figure 2. (a) Varnish film based on colophony - reference (x180); (b) the effect of chemical pollution with SO_2 on the colophony varnish (x180).

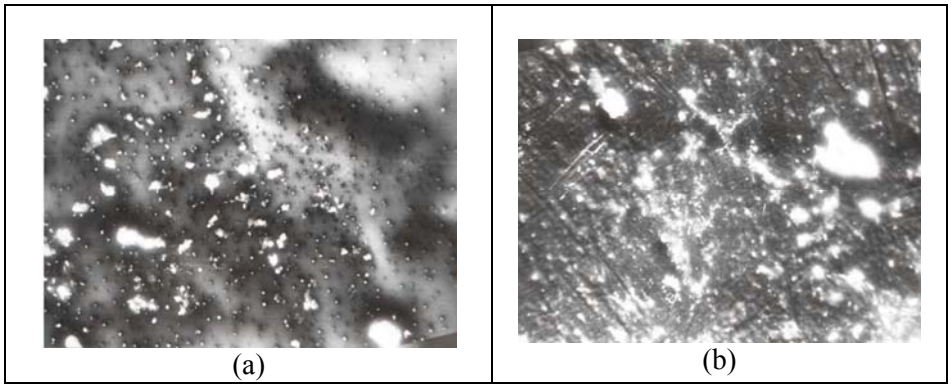

Figure 3. (a) Varnish film based on dammar - reference (x180); (b) the effect of chemical pollution with SO_2 on the dammar varnish (x180).

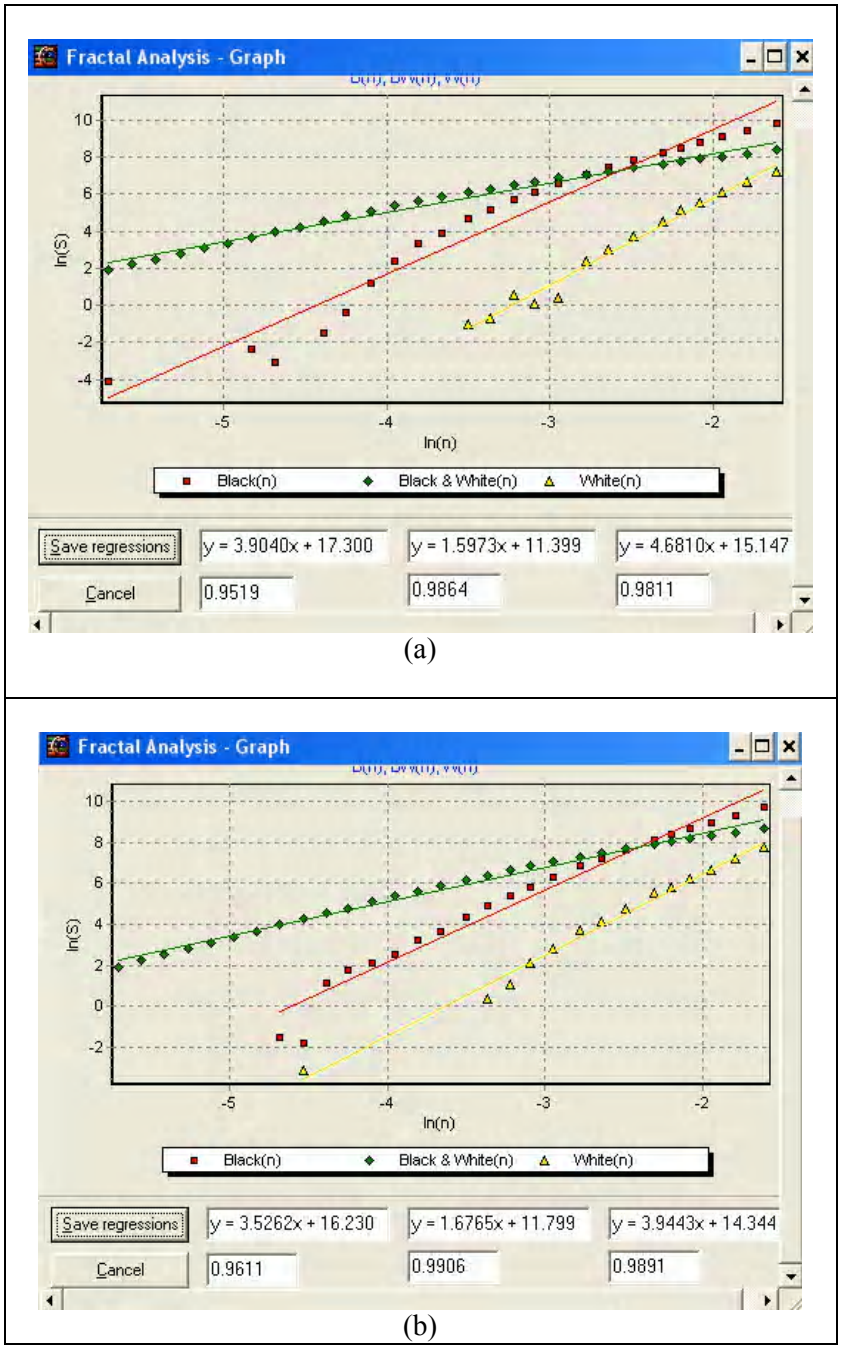

Figure 4. Fractal dimension for shellac film: (a) reference; (b) polluted with SO_2.

Table 1. Fractal dimension for studied resins samples.

Nr.	Sample	Fractal dimension
1	Shellac films	1.5495
2	Shellac films polluted with SO_2	1.6808
3	Colophony films	1.3319
4	Colophony films polluted with SO_2	1.0404
5	Dammar films	1.2785
6	Dammar films polluted with SO_2	1.4527

This behaviour is confirmed by the study about the quantity of water vapours adsorbed by the sample kept in noxious medium [3]. One observed that the value of the ratio $Q = m_{water}/m_{sample}$, between the adsorbed water mass and the sample mass, in the case of varnish films based on colophony exposed in a gaseous medium with a controlled concentration of 0.1mg/L SO_2 is ten times higher than that of the varnish films based on shellac.

These films have a different behaviour in the rich sulphur dioxide atmosphere that comes from different structure. The colophony composition is a mixture of etheric oil and resin acids with unsaturated chains, like abietic acid. This resin suffers chemical changes by introduction of some hydrophilic sulphonic groups at the double bonds, determining rearrangements in the composite structure.

On the other hand, the principal component of shellac is a saturated acid (9, 10, 16-trihidroxypalmitic acid) which do not contain C=C bonds. Dammar resins contain natural polisacharides which also have not C=C bonds, but glicozidic bonds. Then SO_2 pollution produces micro-cracks which induces the increase of fractal dimension. By contrary, colophony films exposed to SO_2 have a decreased fractal dimension and high capacity to retain water.

4. Conclusions

In this work we sustained the usefulness of knowledge of modifications of some physical characteristics produced inside natural materials when they are maintained in polluted atmosphere. From the point of view of sensibility to SO_2, it is recommended that shellac and dammar films should be used by painters.

This fractal analysis conclusion is confirmed by the study about the quantity of water vaporous adsorbed by the sample kept in noxious medium.

Fractal analysis is a new method for surface science. It can contribute to a better understanding of the influence of the polluted atmosphere on varnish films properties and, as a consequence, on the beauty of pictures.

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