# NEW ANTICORROSIVE PROTECTIONS FOR THE ROTATORY AIR PREHEATERS IN ENERGETICAL INSTALLATIONS

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*The cellular bodies placed in the cold heat exchange area of the rotatory air preheaters from energetic installations are strongly affected by the sulphuric corrosion. They can be protected using performing film forming coatings combining thermal, erosion, anticorrosive resistances, flexibility, adhesion and thermal conductivity.*

*Insuring a high degree of performance parameters determined structural modification of some thermosetting polymers from epoxy resins category through esterification with fatty acids to increase elasticity and with acryl monomers to improve chemical and thermal resistance and adhesion. Micro and nanostructured metallic powders with varied morphostructural characteristics were obtained on a humid path - by treating metallic salts with reducing agents specific for the metal - and were characterized by X-Ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), Thermal Analysis, Scanning Electron Microscope (SEM), Thermal Diffusivity/ Conductivity..*

*Organometallic film forming compositions were obtained and analysed to determine the efficiency of the polymeric system and metallic powders dispersed in its matrix. Obtaining a stabilised and compatible system was done in function of the high specific weight of metals and reduced steric stability of suspensions, dispersion system viscosity which contribute to stabilization, metal compatibility with dispersion constituents which determine powder dispersability, and optimal powder concentration.*

*Experimental tests followed stabilization of film forming protections in corrosive atmosphere which combine thermal and chemical resistance and reproduces as close as possible the exploitation conditions. Thermophysical determinations mark out in what extent, the obtained protection assures a thermal conductivity close to the metal, and the comparative analysis of diffusivity of films*

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*which incorporate metallic powders at different levels, associated with the economy criteria, lead to selection of the best variant.*

*Researches regarding obtaining of new anticorrosive compositions are oriented towards optimization of exploitation activities in energetic installations, through the need to use some performant and sustainable materials which must insure efficient protection of rotatory air preheates, but do not significantly modify the heat transfer process.*

**Keywords:** corrosion, rotatory air preheaters, modified polymers, metallic powders, organo-metalic systems

## 1. Introduction

Cellular bodies placed in the cold heat exchange area of the rotatory air preheaters from energetic plants are strongly affected by the sulfuric corrosion [1]. Protection can be made with organo-metallic coatings with performing properties: thermal and anticorrosive resistance, flexibility and thermal shock resistance, adherence, erosion resistance and thermal conductivity, not to significantly modify the heating exchange process, preheaters being – from functional point of view – heat exchangers. If the first properties can be imposed to the polymer films based on known structure-properties relations, thermal conductivity can be obtained only by introducing highly dispersed metallic powders [2].

## 2. Experimental part

Anticorrosive coating compositions are based on specific components which confers an optimal equilibrium to critical properties: binding (polymer solution) which insures the forces that maintain the film integrity; powders of some metals with controlled conductive properties; anticorrosive pigments with active barrier properties; additives that controls rheology, improve dispersion in highly pigmented systems, determines a better orientation of metallic pigments; solvents compatible with the polymer, which rapidly adjust viscosity. Choosing the structured components for film-forming composition formulation was made using the known structure-properties relations. Establishing the composition of the mixture consisted in determining the optimal binding/metal ratio, the quantity and nature of the necessary additives for a dispersion with maximum effect. Settling the optimal pigment concentration in order to obtain a maximum thermal conductivity can be made only through measuring the thermal conductivity in function of the pigment concentration for each of the studied resin-metallic powder film-forming systems.

Epoxy resins constitute a versatile thermosetting resins family which can be modified to improve their properties in compared with the initial ones: by esterification with fatty acids [3] to increase elasticity, than with acryl monomers to increase the chemical, thermal and corrosion resistance, adhesion and elasticity [4]. Experimental was proven the fact that the polymeric system, efficient to realize some anticorrosive protection, is the one modified with monomers. The unsaturated esters obtained after the reactions with fatty acids were cross-linked through engraftment with monomers, in the following conditions: with methyl methacrylate and acrylic acid in a monomers/epoxy esters ratio of 1.5/2.0, temperature of $160^0$C, 2% initiator concentration ($J_{12}$ system); with styrene and acrylic acid in a monomers/epoxy esters ratio of 1.6/2.0, temperature of $160^0$C, 2% initiator concentration ($J_{14}$ system); and with butyl acrylate and acrylic acid in a monomers/epoxy esters ratio of 1.6/2.0, temperature of $150^0$C, 3% initiator concentration ($J_{17}$ system).

Nano- and microstructural powders of copper, nickel and silver with flakes and spheric particles shapes have been prepared in aqueous environment in controlled work conditions (pH, temperature, concentration, surface regulators), from metallic salts solutions with specific reducing agents such as formaldehyde, hydrazine, ferrous sulfate. Metallic powders were characterized through X-Ray Diffraction (XRD), Infrared Absorption Spectroscopy (FTIR), Thermal Analysis, Scanning Electron Microscopy (SEM), Thermal Diffusivity/ Conductivity. The comparative analysis of various metallic powders diffusivity (Ag, Al, stainless steel, copper, nickel), together with the economic criteria, lead to the selection of the most accessible solutions for the proposed purpose, such as: Cu = 380-384 $W/m^0K$, Ag = 324-435 $W/m^0K$, Al = 200-215 $W/m^0K$. The silver powders represent the highest level of thermic conductivity which can be accomplished in the polymer-powder system (standard system) and have been used just for comparison in the films thermophysic properties analysis.

To insure the long term anticorrosive protection were used pigments with the role to “passive protection”, enhancing the barrier effect of the coating itself. The iron oxide with lamellar structure, through its high specific gravity leads to the parallel orientation of particles with the surface and forms a network as a barrier against pollutants. A high density of packing into film can be attained through the conjunction of non-lamellar particles with the lamellar ones; in this purpose, micronized pigments as a synthetic mixture of iron oxides and manganese, $(Fe, Mn)_2O_3$, were added. The increased specific gravity of metals and reduced steric stability of suspensions determined the nature of the additives necessary for dispersion with a maximum effect. Cellulose esters in combination with bentonite represent the dispersion environment optimum for metallic pigments, conferring the control of viscosity while keeping the deformation resistance. The two properties, although opposite, can be simultaneously satisfied due to the newtonian flow properties combined with a high molecular weight. The use of dispersion additives is essential for the stabilization of pigment particles during film formation; mixtures of polymeric dispersants with nonionic/anionic character were used.

The study of polymeric-metallic powders matrixes underlined the obtaining of some performances not possible for the individual constituents. The rheologic study of the epoxy resins dispersions having as dispersed phases metallic powders, emphasizes the interactions between them, determining the specific behaviour of each system. This study was performed with a Haake VT 550 rheoviscosimeter with the following configuration: sensor system $S_3$(MV1), measuring domain $d_1$ and $d_2$, shearing speeds interval, $\dot{\gamma}$, between 1.17 and 1872 $s^{-1}$. Measurements were done at the temperature of $25 \pm 0.1^0$C, with a thermostating time of 20 minutes. The thermal conductivity tests were done according to ASTM E1461 specifications. The used device was the Flashline 3000 apparatus, capable of determining with an incertitude of ± 2.1 % for 95% degree of confidence.

## 3. RESULTS AND DISCUSSIONS

Processing the film-forming compositions which contain epoxy modified polymers and metallic powders pursued two directions:

- the effect of metallic pigments in the optimization of the thermal conductivity coefficient of the polymers system. In this purpose, metallic pigments were introduced in variable percents, 30%, 40%, 50%, 60% from the volume of deposition in different forms to form a continuous network on the polymer section. Proving that the thermal conductivity of the polymer/metallic powders systems has values between the two limits of the mixtures law, Ziebland [5] suggests the use of an arbitrary relationship of the type:

$$\lg \kappa_c = \nu_p \lg \kappa_p + \nu_m \lg \kappa_m \quad (1)$$

  where $k_c$ and $k_m$ are the thermal conductivities of the system and matrix, and $k_p$ is the hypothetical thermal conductivity of the metallic powders, very important elements for the mechanism of conduction through pigment particles and the polymer which forms the conductive coating protection system
- determination of the compatibility between the polymeric matrix and metallic powders. With this purpose, the metallic pigments finely dispersed, paste or flacks, were incorporated in polymers, studying the properties exposed in polymeric systems (size, porosity, shape, packing, orientation mode and dispersion), the influences on the possibility to form some cracks, nature of interface bonds, thermal transitions which influence the modification of the physical properties

Pigment dispersion in the binder requires the stimulation of bonds, respectively, of the forces which exist in the dispersion to counteract the action of gravity on pigments and brownian movement on binder. The very fine solid particles can be incorporated in fluids through high speed dispersion, obtaining colloidal suspensions; a characteristic of these is that the small, fine particles do not settle under the action of the gravitation force. The best results of dispersion were obtained with the DISPERMAT technology (VMA-GETZMANN GMBH-Germany), through the introduction of the greatest mechanic strength possible for tangential speeds of 18-25 m/s, with the induction of the "doughnut" effect (laminar flow). The different viscosity of the polymers, charging degree, metallic powders particles sized determined the settlement of some stages/differential working parameters to insure the optimal predispersion/dispersion. The correlations established between the dispersion parameters (energy, ingredients, equipment) and the dispersion degree can develop empiric relationships which allow the optimization of performances and theories which explain the compositions behavior.

Film-forming compositions are complex rheologic systems for which is necessary to know the apparent viscosity, plastic behavior, flowing effort, thixotropy, variation of the apparent viscosity with the shearing speed and expansion. From rheological point of view, none of the components – dispersion environment (butanolic solutions of epoxy resins) or disperse phase (metallic aluminum flake powders, paste, as well as highly dispersed copper) – does not impose certain characteristics, but there are certain interaction between those, which leads to specific behavior of each system. Butanolic solution of epoxy resin $J_{12}$ as disperse medium leads to film-forming system with ideal plastic fluid behavior at low shearing tensions, when disperse phase is constituted of aluminum, and pseudo-plastic when is constituted of copper. The highest dynamic viscosity was obtained in the film-forming system that contains as a disperse phase copper powder, followed by the one that contains flake aluminum, and the lowest for the paste aluminum. Dispersions that contain flake and paste aluminum are thixotrope and have a practically complete structure restoration at low shearing speeds, while the other one have a time independent rheological behavior. When the disperse environment is the butanolic solution of epoxy resin $J_{14}$, film-forming system with flakes aluminum as a disperse phase is the only one that has an initial pseudo-plastic behavior, for all the others this being ideal-plastic. Viscosity values are higher for each of the disperse phases, excepting the system that contains paste aluminum, for which this is responsively lower. In $J_{17}$ epoxy resin solution used as a disperse medium, flake and paste aluminum, as well as copper powder lead to initial pseudo-plastic behavior dispersions, less pronounced for the last one, followed by ideal-plastic. Viscosities have highest values, especially for aluminum based dispersions for which determinations were made. Film-forming system that have aluminum as a disperse phase show a weak thixotrope behavior, while the one that contains copper does not show a time dependent rheological behavior.

Organo-metallic systems were applied on metallic samples (RCA37), diffusivity/ thermal conductivity dependence with temperature being determined. Thermophysic determinations showed in what measure the realized protection insures a thermal conductivity as closed to the metal as possible, so that the heat exchange of the rotatory air preheaters would not be significantly modified. Low emissive covering application leads to radiation reduction in the heat flow along covering and therefore in thermal conductivity decrease. The decrease ratio depends not only on the number of coatings and their emission but also on the based material properties, its thermal conductivity, optical thickness and medium temperature. This contributes to the complex behavior of the coatings. The effectuated determinations regard a heat flow analyses through conductive coatings. Different factors that affect apparent thermal conductivity was analyzed and the choice of conductive particles contain was optimized. Heat flow measurement was made by thermal diffusivity determination on the samples covered with resins that contain conductive materials (Ag, Al, Cu) in various proportions. The thermal diffusivity difference between the covered materials was established, to settle thermal transfer decrease proportions (percentage) in the covered materials, compared to the non-covered base material. It was proved that using an increasing proportion of particles in resins lower thermal transfer reduction, and the obtained differences on the materials that particles are made from decrease proportionally (figure 1)

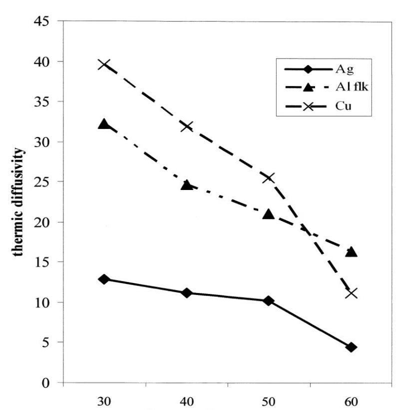


Figure 1: The lowering of thermal transfer function of metal charging degree

Porosity, the exposed properties in polymeric systems, particles compacticity, and dispersion are very important elements when conduction mechanism through pigments particles and the polymer that forms the conductive coating protection system are considered. Best results were obtained at a 60% metal ratio (for silver it was obtained a 4% decrease, comparing to copper for witch a 11% decrease was obtained). A decrease below 15% is acceptable and does not significantly influence transfer at the level of heat exchange process in the rotatory air preheaters. Particles distribution in the resin mass was observed through electronically microscopy images for the coatings added with a 60% metallic pigments ratio. At higher exposures conductive bridge forming between particles from the resin it is noted. Thus, introducing a higher particle ratio in the resin mass will lead to optimal conditions for increasing thermal transfer through covered samples, lowering to the minimum heat lost.

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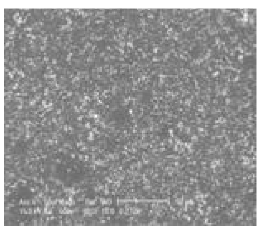
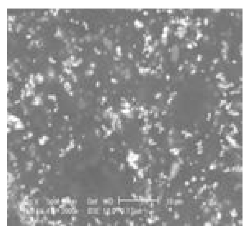
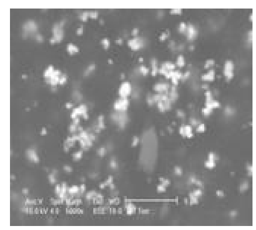
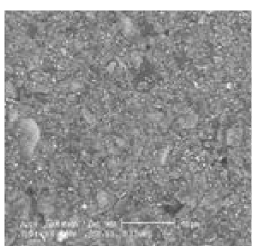
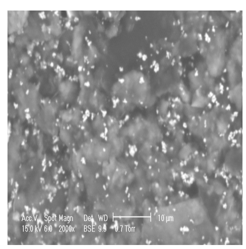
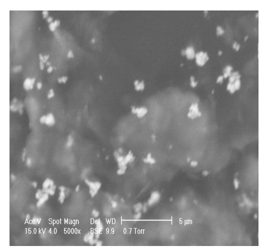
| <br>Film-forming system with copper (magnitude 500x) | <br>Film-forming system with copper (magnitude 2000x) | <br>Film-forming system with copper (magnitude 5000x) |
| <br>Film-forming system with aluminum flake (magnitude 500x) | <br>Film-forming system with aluminum flake (magnitude 2000x) | <br>Film-forming system with aluminum flake (magnitude 5000x) |

Experimental tests followed stabilization of film forming protections in corrosive atmosphere which combine thermal and chemical resistance and reproduces as close as possible the exploitation conditions. Accelerated tests (according SR EN ISO 3231) have selected adherent, compact, but also flexible structures. The compatibility between the polymeric matrix and the mettalic powders has been highlighted due to the increas of the quantity of metal, through the visible improvement of the anticorrosive properties of coating.

## 4. Conclusions

Metallic powders with controlled conductive properties, highly disperse, paste or flakes, were dispersed in epoxy polymers modified with acrylic monomers, along with anticorrosive pigments, solvents, additives, that confers an optimal equilibrium of the critical properties. Film-forming composition formulation had pursued the introduction of a high pigment concentration in the polymeric dispersion, rheology optimization for a long time stability, a high compatibility between system components.

The study of polymeric-metallic powders matrixes underlined the obtaining of some performances not possible for the individual constituents.

The rheologic study of epoxy resin dispersion, having as disperse phase metallic powders, points out the interactions that determine specific behavior of each system.

By adding metallic powders to the polymers, these will begin to take over metals thermal properties, according to the introduced proportion. Using increasing proportions of particles in the resin leads to real improvement of the anticcorosive protection, mass will reduce thermal transfer lowering, and the differences obtained between the materials that particles are made from decrease proportionally.

Best results were obtained in a 60% metal ratio, for which a thermal transfer lowering under 15% is obtained, that is acceptable and does not significantly influences the heat exchange process in the rotatory air preheaters.

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