



# The effect of amorphous chalcogenides on mechanical and anticorrosive properties of protective organic coatings containing high amounts of zinc metal particles

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## ABSTRACT

The objective of this paper concerns reduction of zinc metal content in organic coatings while preserving their high anticorrosive efficiency. The two goals can be achieved by using amorphous chalcogenides as components of the protective coating. Special attention was paid to materials containing Ge<sub>20</sub>Se<sub>80</sub>, Ge<sub>30</sub>Se<sub>70</sub> and Ge<sub>40</sub>Se<sub>60</sub>, which were characterized by physico-chemical properties. An epoxy ester resin was used as binder for the investigated organic coatings. Organic coatings were prepared by combining zinc metal with amorphous chalcogenides. The resistance of the prepared films was evaluated using the results of mechanical tests. The anticorrosive efficiency of the prepared films was evaluated using the results of direct corrosion tests. Thus the following conclusion can be made from the results of anticorrosive tests: the higher the pigment volume concentration of amorphous chalcogenides in the coatings, the higher the protective performance of the paint against corrosion.

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## 1. Introduction

Covering with anticorrosive coatings is the most widespread way how to protect metals. The paint film acts as a physical barrier between corrosive electrolyte and steel substrate [1–3]. Anticorrosion paints are two-phase systems consisting of an organic binder and an anticorrosion pigment dispersed in the binder. An anticorrosion pigment is a powder which, when present in an organic binder, has a corrosion-inhibiting effect [4]. Among prominent anticorrosion pigments are, for instance, chromate pigments, which, however, are toxic and harmful to the environment [5–7]. For this reason they are being replaced by phosphate [8–10], molybdate [11], borate [12] or vanadate (IV) [13] pigments. Alternatively, metallic pigments (zinc metal) can be used in the anticorrosion paint formulas [14].

Zinc metal has been already used in anticorrosive coatings for many years as the so-called “sacrificed electrode” [15–17]. Corrosion products formed in cathodic protection block the pores present in the film and, accordingly, reduce its conductivity, resulting in the electrochemical mechanism being replaced by the barrier mechanism [18]. An active protection is concerned since the function

of electrochemical cathodic protection takes place upon mechanical damage to the coating [16,19,20]. The maximum anticorrosive protection is achieved when the condition of equilibrating pigment volume concentration (PVC) with critical pigment volume concentration (CPVC) has been satisfied during the preparation of the coating [21]. However, a high volume concentration of zinc metal has a negative effect on both the mechanical properties of the organic coating and its adhesive capacity [19]. Other problems arise during the production of highly pigmented coatings; rheology of such systems is not appropriate for the application techniques and the coatings have poor leveling. At the same time, storage of liquid paints is accompanied by the sedimentation of zinc particles. The sedimentation is not caused only by the rheology parameters, but also by high specific density of zinc metal [15].

Amorphous chalcogenides consist of S, Se or Te in combination with suitable elements – As, Ge, Ga, Sb and others [22]. In the last decades, considerable attention has been devoted to chalcogenide glasses and amorphous thin films owing to their exceptional electrical and optical properties. Their interesting (mainly optical) properties such as broad transmission window, large refractive indices values, large optical non-linearity, etc. are applicable not only in different fields of optics and optoelectronics [23–26], but also potentially in other fields, among them in coatings in order to enhance the quality of the organic protective coatings. We had already demonstrated a positive effect of amorphous chalcogenides

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on the formation and properties of the oxypolymerising drying paint films [22]. When  $\text{Ge}_{30}\text{Se}_{70}$  and  $\text{Ge}_{30}\text{Se}_{70}$  chalcogenide glasses were compared, better results were achieved for the latter composition [22]. As next logical step, the effect of chalcogenide glasses from Ge–Se system (differing in their chemical composition) on the potential reduction of zinc metal volume concentration in organic coatings, while preserving their high anticorrosive efficiency, is studied in this work.

## 2. Experimental part

### 2.1. Synthesis of $\text{Ge}_{20}\text{Se}_{80}$ , $\text{Ge}_{30}\text{Se}_{70}$ and $\text{Ge}_{40}\text{Se}_{60}$ glasses

Samples of  $\text{Ge}_{20}\text{Se}_{80}$ ,  $\text{Ge}_{30}\text{Se}_{70}$  and  $\text{Ge}_{40}\text{Se}_{60}$  glasses were prepared by direct synthesis from high purity germanium and selenium (99.999%) using melt and quench technique.

Quartz ampoules to be used for the synthesis of the glasses were first purified: the ampoules were filled to the rim by aqua regia and left to stand for 24 h. The ampoules were then rinsed four times with demineralized water and dried in an oven at 105 °C.

Individual components were then weighed into the purified ampoules in amounts corresponding to the specified molar ratio of the two elements. The ampoules filled with the material were evacuated to residual pressure  $<10^{-3}$  Pa and sealed off from the vacuum source. The synthesis took place in a rocking tube furnace at 970 °C for 20 h. Perfect homogeneity of the melt was ensured by continuous rocking of the furnace. All glasses were prepared by dropping the ampoules containing the melt into cold water (quenching).

Immediately after quenching, the glasses were kept for 2 h in an oven heated to a temperature 30 °C lower than the respective glass transition temperature. The glasses were then slowly cooled (at about 1 °C per minute) to ambient temperature. The reason for annealing and slow cooling was to remove the internal stress from the synthesized glasses.

The composition of individual glasses was checked by electron microscope JEOL JSM-550LV with an energy dispersive X-ray microanalyzer (IXRF Systems). The measurement error was  $\pm 0.5$  at.%.

### 2.2. Grinding of $\text{Ge}_{20}\text{Se}_{80}$ , $\text{Ge}_{30}\text{Se}_{70}$ and $\text{Ge}_{40}\text{Se}_{60}$ glasses

The prepared glasses were subjected to highly efficient grinding in a planetary ball mill at 400 rpm. 20 g of fabricated, pre-crushed chalcogenide glass was loaded into the cylindrical zirconium vessel, then corundum balls and 100 ml of ethanol were added. The grinding time was set at 15 min.

After the grinding, the chalcogenide glass powder was first separated from the corundum balls by means of a sieve. The pigment was then filtered off using a Buchner funnel, washed with 200 ml of ethanol and dried – first for 24 h in air and then in an oven at 105 °C. The glass powders were then used as pigments.

### 2.3. Specification of the pigments employed

Morphology of the zinc metal,  $\text{Ge}_{20}\text{Se}_{80}$ ,  $\text{Ge}_{30}\text{Se}_{70}$  and  $\text{Ge}_{40}\text{Se}_{60}$  particles was determined by electron microscopy (JEOL – JSM 5600 LV, Japan). 2% suspensions of the pigments in redistilled water were then prepared and values of pH and conductivity were followed for 21 days. The CPVC of the pigments was calculated from the density (determined using Autopycnometer Micromeritics 1320) and oil absorption (determined according to the Czech State Standard (CSS) 67 0531 using the “pestle – mortar” method [27]). Determination of particle size and the distribution of pigment particle size were identified by means of Mastersizer 2000 (Malvern, Instruments Ltd., UK) that is able to measure the distribution of particles sized from 0.01 to 2000  $\mu\text{m}$ . X-ray diffraction

(XRD) data were obtained with D8-Advance (Bruker AXE) diffractometer with Bragg–Brentano  $\theta$ – $\theta$  geometry using  $\text{CuK}\alpha$  radiation. XRD data were collected at room temperature from 5 to 70° ( $2\theta$ ) in 0.02° steps with a counting time of 3 s per step.

### 2.4. Formulation and preparation of organic coatings

As a convenient binder, the epoxy ester resin was used. Organic coatings were prepared by combining zinc metal with  $\text{Ge}_{20}\text{Se}_{80}$ ,  $\text{Ge}_{30}\text{Se}_{70}$  and  $\text{Ge}_{40}\text{Se}_{60}$ , using the PVC=0.5%, 1% and 3% and zinc metal volume concentration (PVC/CPVC) equal to 0.67. To compare the results obtained with amorphous chalcogenides, an organic coating containing only zinc metal (at PVC/CPVC=0.67) was prepared. Organic coatings were dispersed using Disolver-type equipment at 4000 rpm for 40 min. The specifications of used epoxy ester resin are as follows.

Commercial name,	WorléeDur D 46, Worlée-Chemie GmbH,
manufacturer:	Germany
Composition:	WorléeDur D 46 is a short oil epoxy ester based on conjugated drying fatty acids
Technical data:	Content of epoxy resin approx. 60%
	Oil content approx. 40%
	Acid value, DIN EN ISO 3682 max. 4
	Delivery form 60% in xylene
	Density 0.98 g/cm <sup>3</sup> (20 °C)

### 2.5. Mechanical properties of the coatings

The physico–mechanical quantities point out the flexibility, the elasticity and the strength of the paint film. These tests provide a basis for studying the mechanism of protective organic coatings action. The evaluation of physico–mechanical properties was carried out after application of the coating onto steel panels (152 mm  $\times$  75 mm  $\times$  0.8 mm, standard low-carbon steel panels S-36, Q-Lab Corporation). The dry film thickness (DFT) was measured using the magnetic gauge in accordance with ISO 2808 [28].

The mechanical properties of coating systems were evaluated according to following standards.

#### 2.5.1. The surface hardness of the paints by pendulum apparatus (ISO 1522)

The hardness of the paint film was determined by means of a pendulum according to Persoz. The results are indicated as per cents related to the hardness of glass standard [28].

#### 2.5.2. The degree of the adhesion of the coatings by lattice method (ISO 2409)

Determination was made using a special cutting blade with cutting edges 2 mm apart and involved the degree of adhesion of the created 2 mm  $\times$  2 mm squares to a base substrate [28].

#### 2.5.3. Impact resistance (ISO 6272)

The test revealed the height of the free fall of a weight (1000 g) at which the paint film still resists to damage. The test was performed on the reverse of the panel with a coating [28].

#### 2.5.4. The resistance of the coating against cupping in Erichsen cupping tester (ISO 1520)

The objective of this test is to identify the resistance of the paint film against ongoing deformation of a coated steel panel with a pressed-in 20 mm steel ball. The result of the test gives so-called cupping in mm during which the first disturbance of the coating occurred [28].

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