INFLUENCE OF INTUMESCENT INORGANIC POLYMER ADDITIONS ON THE FIRE BEHAVIOR OF PAINTS BASED ON ORGANIC RESINS

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This paper presents the fire behavior of intumescent paints obtained by the mixing of various types of intumescent inorganic polymers with resin-based (acrylic / epoxy / polyurethane) paints. The intumescent inorganic polymers were obtained by the alkaline activation of a waste glass powder with / without different types of additives (slag, borax and Na_2CO_3*).*

These paints were applied on metal plates and tested in direct contact with a flame; the coatings exhibited intumescence (volume increase) followed by melting or partial exfoliation of the coatings, for some compositions. These coatings prevented the rapid increase of the metal substrate temperature when put in direct contact with the flame; the addition of inorganic polymers in the paints recipes also prevent the burning of the paint film with open flame and noxious gas emissions.

Keywords: inorganic polymers, intumescence, fire-proof, alkali activated materials, waste glass, acrylic paints

1. Introduction

Every year, worldwide, fire causes injuries and deaths or could result in severe loss of properties. Therefore, integrity and structural stability are key aspects of the fire safety strategy [1]. For the construction based on steel structure, the integrity of structures can be compromised both during and after a major fire event, because steel exhibits a significant reduction of the strength and rigidity at high temperatures. At 550–600°C, the steel used for the structure retains about 50% of its resistance to ambient temperature [1]. Therefore, in many cases, passive fire protection is used to delay the rise in temperature of the steel structures.

In this respect, intumescent coatings became one of the preferred choices due to their numerous advantages, among which ease of application, light weight, and pleasant appearance, are the most important [2]. When exposed to heat/flame, these coatings can swell up to 100 times their original size. Thus, a multicellular

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carbon layer is formed on the surface of the steel structural element and helps to restrict the heat transfer from the hot gases (flame) to the steel substrate. With the protection provided by intumescent coatings, the steel structure can withstand exposure to fire without deteriorating (loss of mechanical strength) for 1–3 h. This extends the time available for saving lives and preserving properties [3].

Intumescent coatings based on inorganic polymers (geopolymers) are promising materials for fire protection, in the case of constructions with steel structures. Previous obtained results proved that it is possible to obtain intumescent materials by alkaline activation with a NaOH solution of waste glass powders [4]. The use of additives such as red mud, fly ash, slag or borax changes the temperature at which is activated the intumescence phenomenon [4-9]. Such materials can be used to obtain intumescent coatings for metal (steel) and other types of substrates (plasterboards) [10]. The main drawback of this type of coating is, for some compositions, a rapid increase in the fresh paste viscosity [9] or a longer setting/ hardening time of the coating.

Preliminary results show that the dispersion of an intumescent material (obtained by the alkaline activation of waste glass powder with/without additives) in silicate paint [6] or in an acrylic paint [11] and its application on steel substrate, can reduce the temperature of the metal substrate when the coated element is in direct contact with a flame. In this respect, this paper presents the fire behavior of several compositions of intumescent paints, based on different types of resins (acrylic, epoxy and polyurethane), in which were added intumescent powders, obtained by alkaline activation of waste glass powder without/with additives.

2. Materials and methods

In order to prepare the intumescent paints, 4 types of intumescent materials were obtained by the alkali activation with NaOH solution of a waste glass powder (WGP) obtained by the fine milling of mixed colors soda lime glass cullet (G) or a mixture of waste glass powder and slag (GZ) [5,6]. GN is the intumescent material resulted by the alkaline activation with a NaOH solution of a mixture of WGP and Na_2CO_3 and GB results by the alkaline activation of a mixture of WGP and borax [6-11]. For these 4 types of materials the intumescence phenomenon occurs at different temperatures - G (~900^{o}C); GZ (~1000°C); GN (~800^{o}C) and GB (~450^{o}C). This is due to the influence of the additives used - Na_2CO_3 (N) and borax (B) additions decrease the activation temperature of the intumescence phenomenon [8-10] opposite to slag addition (Z) which increase the activation temperature [5].

As previously presented, WGP was obtained by the fine grinding a glass culet (mixed colors) in a ball mill. The intumescent material G was obtained by mixing glass powder with NaOH solution (WPG:NaOH=14:1; water to solid=0.45); the resulting paste was stored for 24 hours at 60°C and then in the air at 20°C for 13 days. GZ (WPG:NaOH:Z=11:1:3, water to solid=0.44), GN (WPG:NaOH:N=11:1:3, water to solid=0.34) and GB (WPG:NaOH:B=4:1:4, water to solid=0.34) were obtained in the same way, by mixing WGP with the above-mentioned additives and with the NaOH solution. GZ and GN pastes were cured in the same condition as G, only GB paste was cured for 14 days in air, at 20°C. The hardened pastes were ground in a ball mill to obtain fine powders, which were characterized by laser diffraction particle size analysis by means of a Mastersizer 2000 apparatus, equipped with dispersion unit Hydro 2000 MU (ultrasonication time - 1 min, rotational speed of the pump - 2500 rpm).

Each powder was dispersed in binder, thus obtaining 4 paints (A_G, A_GB, A_GN and A_GZ) – table 1. Other 3 paints (P1, P2 and P3) based on acrylic resin with combinations of 3 or 4 intumescent materials, were also prepared (see table 1).

An acrylic resin, Acronal LR 9014 (BASF), was used as a binder, which is a fine sized, hydrophobic aqueous dispersion of a multiphase straight acrylic copolymer with a tailor-made morphology, of medium viscosity, with a solid content of 45%. Dispersing agent Dispex AA 4040 (BASF) is a solution of an ammonium salt of an acrylic polymer in water, especially suitable for the dispersion of inorganic pigments.

Table 1

Composition of acrylic resin paints with addition of intumescent inorganic polymers

Paint	G, %	GB, %	GN, %	GZ, %	Acrylic resin, %	Water, %	Dispersant DISPEX AA4040, %
A	-	-	-	-	100	-	-
A_G	42.6	-	-	-	29.8	25.5	2.1
A_GB	-	42.6	-	-	29.8	25.5	2.1
A_GN			42.6		29.8	25.5	2.1
A_GZ				42.6	29.8	25.5	2.1
P1 (G+GN+GB)	13.6	15.4	13.6	-	29.8	25.5	2.1
P2 (G+GN+GZ)	13.6	-	15.4	13.6	29.8	25.5	2.1
P3 (G+GN+GZ+GB)	10.65	10.65	10.65	10.65	29.8	25.5	2.1

The viscosity of the acrylic paints was determined using a Brookfield viscometer Byko-Visc Basic H (Byk - Gardner), disk spindle RV#4, at 20 rpm.

The deposition of the paints based on acrylic resin on the metal (steel) plates (100 x100 x 3 mm – length x width x height) was done in two stages. The first stage consisted of deposition of a layer of acrylic resin which was dried in oven at 60°C/20 min; in the second stage a layer of intumescent paint with a thickness of 2 mm was applied on this substrate.

In order to assess the influence of studied intumescent additions on the fire behavior of paints based on polyurethane and epoxy resins, the compositions presented in table 2 were also prepared.

Table 2

Compositions of paints based on epoxy and polyurethane resin with G addition

Paint	G %	Epoxy resin, %	Polyurethane resin, %	Butyl glycol, %	Isobutyl alcohol, %	Thinner, %
E_G	44.2	38.9	-	10.6	6.3	-
P_G	44.2	-	39.9	-		15.9

The epoxy paint E_G was obtained by mixing an epoxy resin E210 -DER 671 (Inchem Germany GmbH) with epoxy equivalent weight of 165-173 grams, butylglycol (BASF), isobutanol (CHIMEXIM) and intumescent material G. The mixture was then homogenized at 10,000 rpm for 30 min to obtain uniform particle distribution. The viscosity of the epoxy paint was reduced by adding to the mixture a proper amount of butylglycol. The application of the paint is done after the previous mixing of the paint with hardener (TETA-Dow Chemical) in a ratio of 3 to 1(weight).

The polyurethane paint P_G was obtained by mixing polyurethane binder Hydra Clear 77(VIRUS), intumescent material G and thinner Hydra Reducer 77 (VIRUS). The mixture was then homogenized at 10,000 rpm for 30 min to obtain uniform particle distribution.

In the case of paints based on polyurethane and epoxy resins, the paint was applied on the steel plate with a brush, in three consecutive layers.

The fire test was performed with a butane torch (Fig.1). The flame was in direct contact with the face covered with the intumescent paint; on the opposite side, the temperature of metal plate was measured with a pyrometer. In all experiments the distance between the torch head and metal plate was kept constant (55 mm).

The mass modification of coated metal plates after the flame test was calculated with the formula:

$$\Delta m = [(\text{Mass } 3 - \text{Mass } 2) / (\text{Mass } 2 - \text{Mass } 1)] * 100\ (\%) \qquad (1)$$

where:

Mass 1 = mass of the metal plate before applying the paint
Mass 2 = mass of the metal plate with the paint film before flame test
Mass 3 = mass of the metal plate with the paint film after flame test.

Fig. 1. Fire test setup

3. Results and discussions

Fig. 2 shows the particle size distribution curve of the waste glass powder (WPG), the precursor used to obtain intumescent materials and Fig. 3 shows the particle size distribution curves for intumescent materials G, GB, GN and GZ.

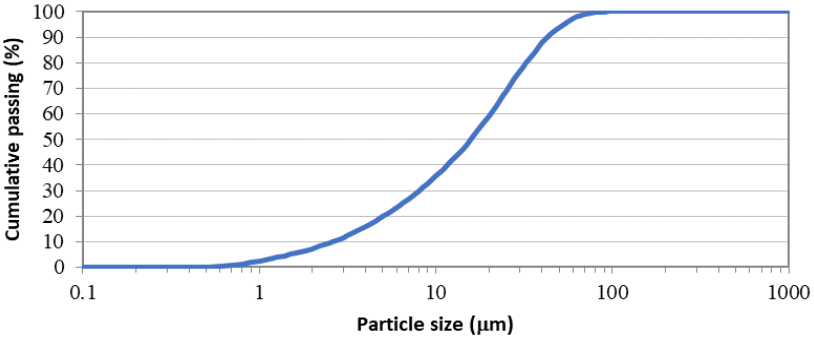

Fig. 2. Particle size distribution curve for glass powder (WGP)

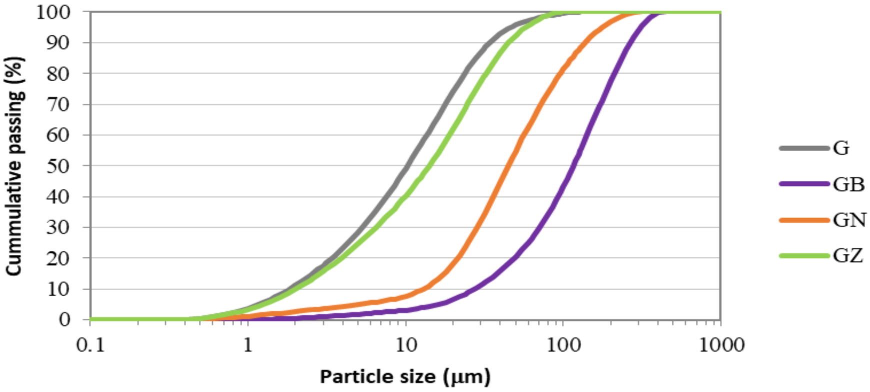

Fig. 3. Particle size distribution curves for intumescent materials G, GB, GN and GZ

As it can be seen from Fig. 3, G and GZ powders have a higher fineness as compared with GN and especially with GB powder; the last one is coarser, mainly because this material has a much lower grindability, having a more pronounced ductile behavior compared to G, GZ and GN which are brittle materials. This behavior is explained by the different composition of GB, as compared with G, GZ and GN; the main component of G, GZ and GN, resulted in the reaction of glass particles with NaOH solution, are sodium and calcium silicate aluminate hydrates (NCASH); in GB, beside this type of hydrates is also assessed the presence of sodium metaborate hydrates resulting from the reaction of borax with NaOH solution [6-8]. The presence of these compounds reduces the mechanical strength of the hardened paste and decreases GB's grindability.

The admixture of intumescent materials (representing 42.6% of the mixture) in the paints based on acrylic resin, determines, as expected, a significant increase of paints viscosity (Fig. 4). The viscosity of intumescent paints varies between 113 and 127 Poise, much higher as compared with reference (acrylic resin - A) which has a viscosity of only 27.5 Poise.

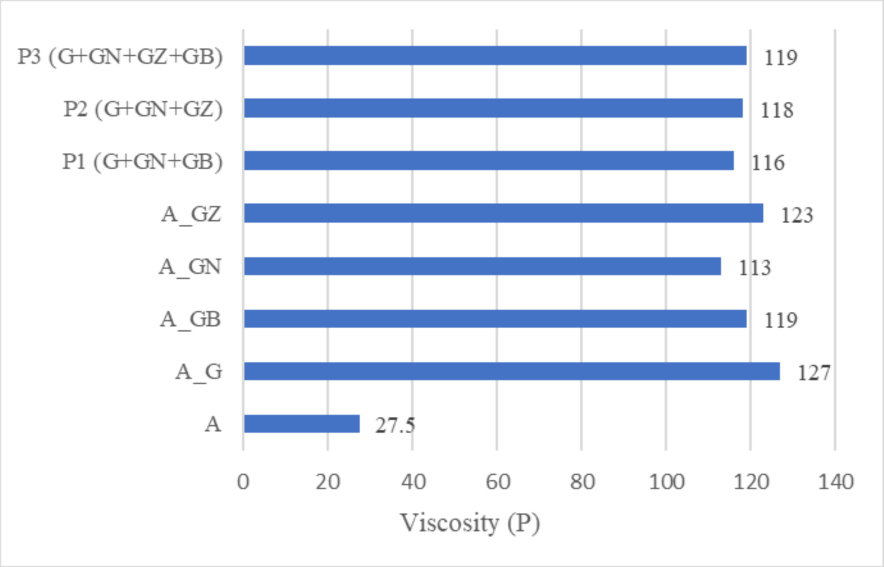

Fig. 4. Viscosity of the paints with/without intumescent inorganic polymer admixtures

For this reason, after drying, the average thickness of acrylic resin-based paint films with intumescent additions, applied on metal plates, is higher as compared with the one of reference paint (A) - see figure 5.

The higher mass loss assessed for acrylic paint A (despite the smaller thickness of the deposited layer) compared to acrylic resin paints with the addition of intumescent materials, is due to the lower resistance to fire of this paint. In the case of paints based on acrylic resin with intumescent additives, even if the phenomenon of intumescence occurs, which causes the swelling of the film (see Fig. 6 - A_GB) and in some cases the peeling and falling of the film on a small portion - see Figs. 6 and 7, however, the mass loss is smaller under conditions of a greater thickness of the paint film. This suggests a better fire behavior of these paints.

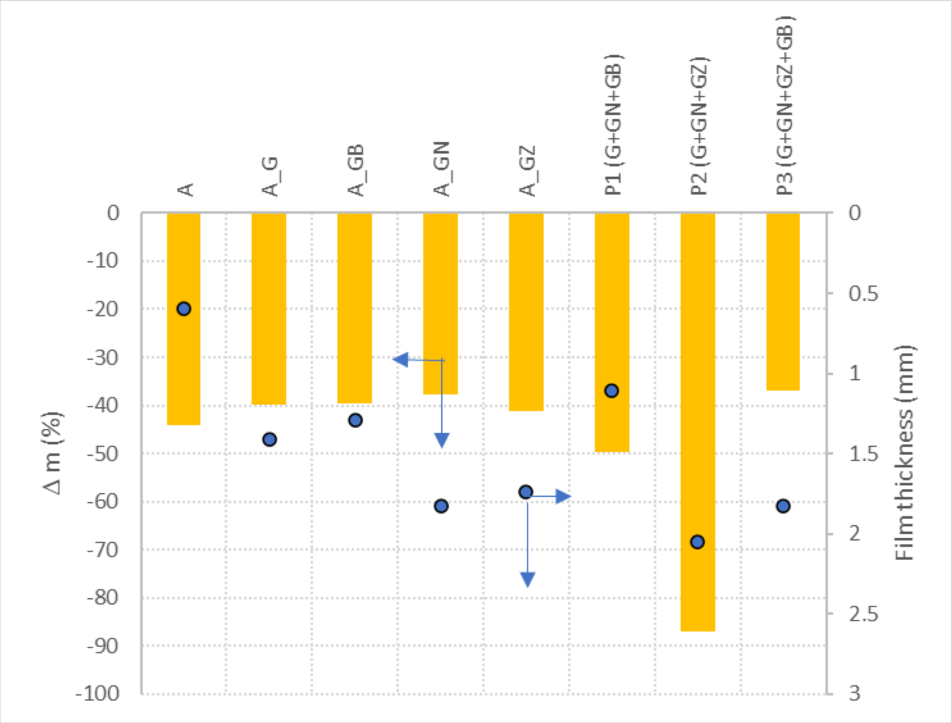

Fig. 5. The thickness of the paint film (after drying, before the test) and the mass loss recorded after the fire test

Figs. 6 and 7 show the visual aspect of the metal plates covered with intumescent paints, before, during and after the fire test. As it can be seen, before the test, all the intumescent coatings had a good adhesion to the metal substrate. It should be noted that in the case of coatings based on acrylic resin with/without intumescent materials additions, no flame or smoke emissions were detected. On the opposite side, the sample coated with epoxy resin paint (E_G - Fig. 7) caught fire and burned with significant smoke emissions, from the first moment of contact with the flame; moreover, the coating changed its color (blackened) and peeled off from the surface of the metal plate (on a significant surface), thus confirming the reduced fire resistance of this paint. The polyurethane-based coating also blackened and peeled off from the surface of the metal plate when put in direct contact with the flame (P_G - Fig. 7). Smoke emissions also occurred during the fire test of this film, but no ignition of this material was observed, as in the case of E_G.

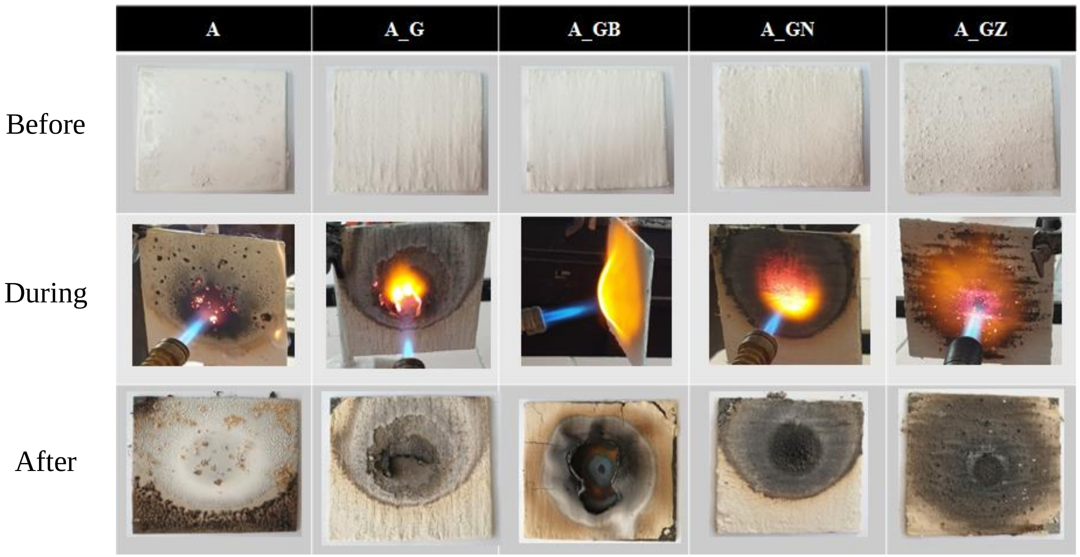

Fig. 6. Visual aspect of metal plates coated with acrylic resin paints (with/without intumescent inorganic polymer addition) before, during and after fire test

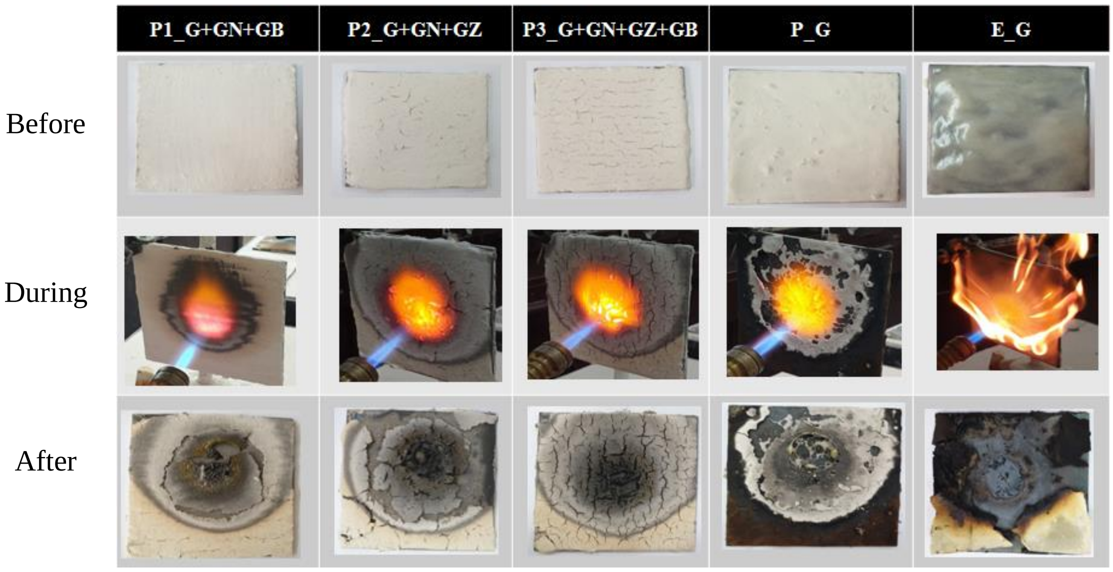

Fig. 7. Visual aspect of metal plates coated with paints with intumescent inorganic polymer addition, before, during and after fire test

One can also notice an increase in the metal plate temperature, measured on the opposite side of the one covered with paint which is in direct contact with the flame (Figs. 8 - 10).

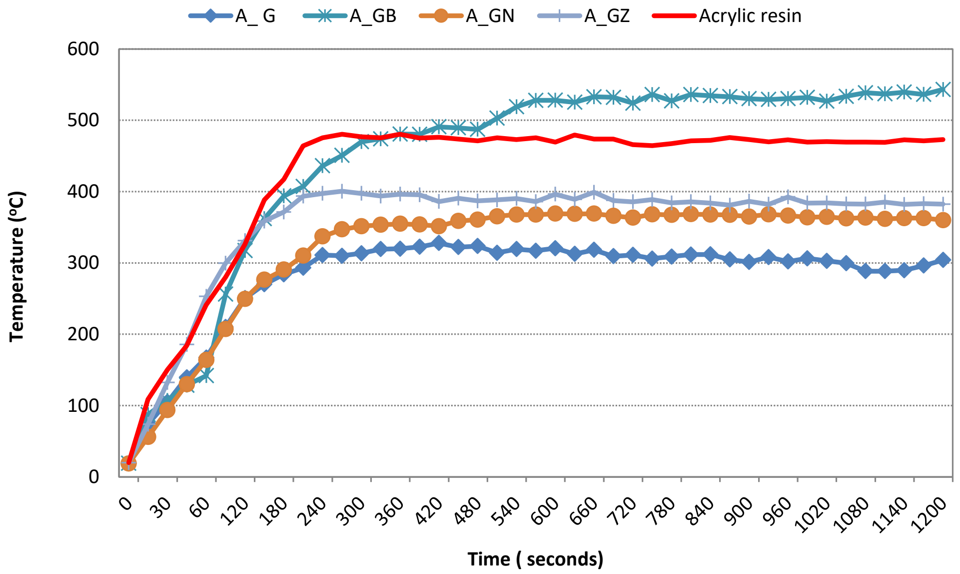

Fig. 8. The substrate temperature of the metal plates coated with paints based on acrylic resin A with/without intumescent materials additions vs. contact time with the flame

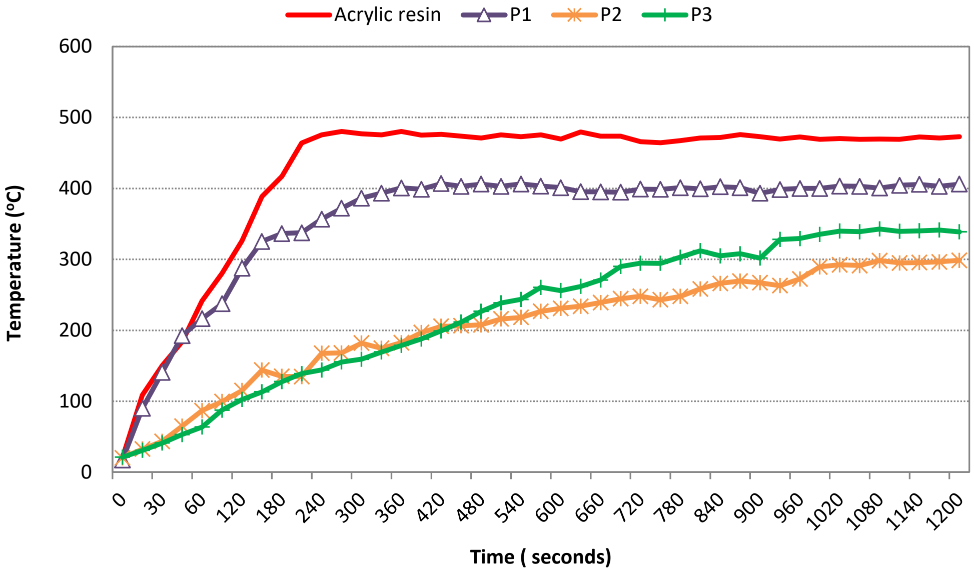

Fig.9. The substrate temperature of the metal plates coated with paints based on acrylic resin A with intumescent material additions vs. contact time with flame; P1 (G + GN + GB), P2 (G + GN + GZ) and P3 (G + GN + GZ + GB)

In the case of paints based on acrylic resin (Fig. 8) the addition of intumescent powders (GZ, GN and G) decreases the rate of temperature increase as compared with reference (acrylic paint - A). In the case of the metal plate with A_GB coating, the increase of the metal plate temperature occurs initially at a lower rate (compared to A) due to the endothermic effect specific for this type of intumescent material [9]; subsequently, as a result of the exfoliation of the coating from the surface of the metal plate, the temperature of the metal substrate increases rapidly and stabilizes at a higher temperature than in the case of reference (A).

The combination of 3 or 4 types of intumescent powders in the compositions of P1, P2 and P3 paints, determines a better fire behavior of these films (compared to paint A) - Fig. 9. P2 and P3 coatings, containing GZ, had a better behavior during the fire test, most probably due to the high activation temperature of the intumescent phenomenon for this material.

The evolution vs. time of the metal plate temperature when covered with paints based on acrylic, epoxy and polyurethane resins with intumescent material G admixture is presented in Fig. 10.

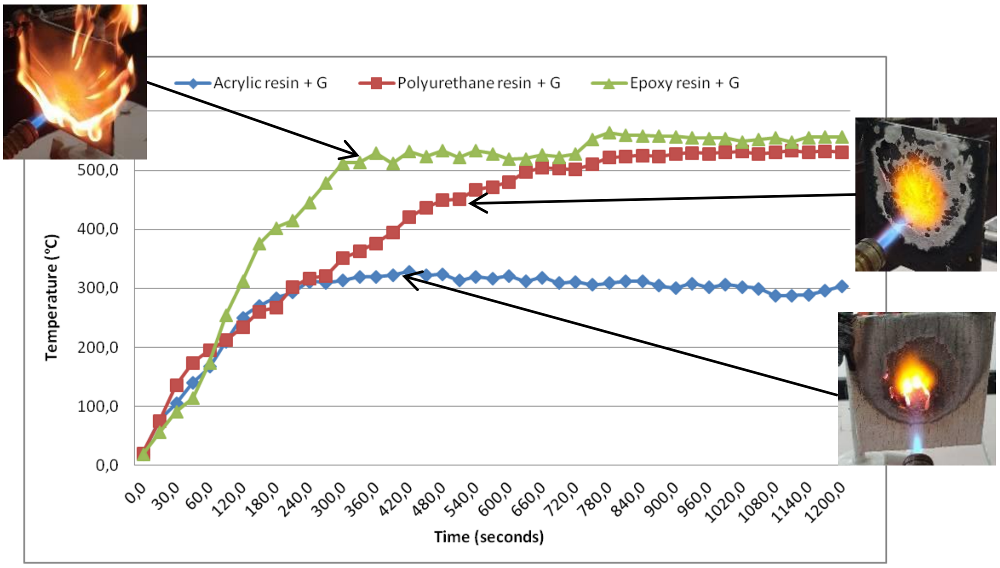

Fig. 10. Temperature of the metal substrate for the metal plates covered with acrylic/polyurethane/epoxy paints with G additions vs. time

As expected, due to the different behavior of these coatings when put in direct contact with the flame, the fastest increase in the temperature is recorded for the composition based on epoxy resin. In the case of polyurethane resin film, there is a slower increase of the cold face temperature (compared to E_G) and the composition based on acrylic resin has a much better behavior i.e., protects the metal substrate more efficiently.

4. Conclusions

Intumescent paints based on various types of resins (acrylic/epoxy/ polyurethane) can be obtained by mixing with intumescent powders resulting from the alkaline activation of waste glass powder with/without various additives.

Intumescent pains based on acrylic resin are more effective in reducing the temperature of the metal substrate during the direct flame test compared to those based on epoxy or polyurethane resins.

The addition of intumescent materials (representing 42.6% of the mixture) in the paints based on acrylic resin, causes a significant increase of their viscosity.

The main drawback of this type of paint is their relatively short shelf life; the paints show a significant thickening in the following two weeks after preparation.

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