ECOLOGICAL FIRE PROTECTION MATERIALS TO INCREASE SAFETY IN ENERGY EQUIPMENTS

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Fire behaviour is a major factor which limits the use on large scale of new materials, presently being developed various materials and technologies in function of the application field. Problems regarding toxicity and heat emission limited the expansion of new materials in sectoral and cross-sectoral applications.

The paper describes the obtaining of new fire protection knowledge based materials, high performant and cost efficient through implementing current scientific and technological knowledges in existent technologies.

Compositions of ecological fire protection materials were obtained, which include gas and nontoxic vapor supplying ingredients that expand the films under fire action and carbon supplying ingredients that insure a solid spinel structure of the foam. Inorganic charges with high thermal resistance, high specific surface and controlled concentration of active surface groups were obtained, following the influence of micro and macrostructural parameters of powders on composition characteristics.

Tests pursued the behavior of obtained films in normal functioning state and in the case of a fire. Fire behavior of ecological protection materials was determined through reduced scale tests, obtaining fire resistances greater than 60 minutes and 2000-5000% expansion indexes.

Keywords: fire protection, thermofoaming coatings, ecological.

1. Introduction

Fire protection represents a constant challenge due to increasingly severe quality and safety requirements imposed on protection materials, as well as the dynamics of new materials appearance used in economy.

The changes occurred in industry imposed finding new more efficient fire protection methods and materials, capable to correspond to insurance exigencies

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on fire security of persons, equipments and buildings. Researches on fire protection did not succeed in insuring clean processing and utilization methods. The existing materials, obtained through the years, according to the existing knowledge, are of a great variety and are created for limited application fields.

The constrains imposed by the UE environmental legislation which comprise the limitation on the use of solvents, heavy metals and chlorinated compounds (due to emissions produced by burning and recycling), determined the obtaining of water dispersed soluble resins based fire protection coatings.

The most used, in EU, coatings and composite materials with low inflammability are still based on halogenated coatings, undesirable from environmental impact point of view. Burning retardants used on a large scale in plastic materials, composite materials and coatings compositions are, in general, halogenated products which produce aggressive emissions in the case of a fire and also recycling at the end of the life time. Bromine and chlorine retardants are persistent chemical substances which, in some cases, can affect the hormonal balance, the unfolded studies proved the impact on the brain activity of children [1]. This is the reason why a part of the bromine retardants were forbidden starting from 2004 [2] and exist the tendency to substitute them with less dangerous products [3].

Although the problems are similar in the entire coating industry (limit the use of solvents and heavy metals for adherence primers), in the case of fire protection materials appear supplementary constrains due to smoke and emissions resulted from burning, for which exists very severe rules adopted on European level. Also, due to the different nature of support surfaces, still was not possible the obtaining of coating materials which can be used for all the substrate types, without requiring intermediate adherence layers and which completely eliminate noxious raw materials from their compositions.

Thus, approach of researches regarding ecological knowledge based fire protection materials is justified and presents importance not just from the scientific and technological progress point of view, but also the social impact through obtaining performant and safe materials, pursuing realization of ecological thermofoaming materials without solvents and chlorine products in their composition and without requiring adherence primers during application.

2. Experimental Researches Regarding Obtaining of Ecological Fire Protection Materials

At ICEMENERG, multidisciplinary elaborate researches were done to obtain ecological fire protection thermofoaming materials, settling some compositions which attain the necessary characteristics for a protection in normal functioning state in all the established application fields, as well as increased fire resistance in the case of a fire.

Ecological fire protection compositions were obtained taking into account the necessary constituents for adhesion on different substrates, insuring cohesion and finding a thermofoaming system to insure the increase of foam in a fire case. Inorganic thermal resistant micro and nanostructural charges were used.

A fire protection thermofoaming system contains the basic elements capable of forming the insulating layer of expanded foam [4,5]: carbon source (carbon donor), acid source (dehydrating agent) and an expansion agent or gas source. As binder and expansion agent, a nonchlorinated agent was used which, in normal functioning conditions, accomplishes cohesion and insures the films continuity and resistance. In the case of a fire, the binder forms a melted film in which gases are evolved and is the supplier of incombustible, nontoxic gases which expand the melted film and insulate the support, preventing burning. The carbon source is constituted of polyols that lose hydrogen and form “solid carbonic foam” with the density and shape great enough to produce sufficient safety in regards to fire expansion. The acid source is comprises ammonia phosphates and polyphosphates which, under the action of heat, decompose and act as catalysts of the carbonic foam formation reaction.

The expanded layer represents a barrier which physically protects the combustible material surface in regards to the heat transfer, acting as a “shield” against flame. This reduces the temperature of the surface in its immediate vicinity, delaying the increase of surface temperature and prevents the oxygen diffusion at the combustion zone. Forming the expanded coal layer has as effect also the reduction of the material quantity which is transformed in volatile combustible. After the appearance of fire, the thermofoaming film expands and forms rigid carbonized foam with a high degree of expansion, adherent to substrates, having thermal insulation capacity for substrates, long term fire resistance and no emission of toxic gases.

Obtaining ecological fire protection thermofoaming materials with such characteristics allows the realization of efficient protections against fire. In all compositions, mineral incombustible charges which form, in the combustion process, a spinellic rigid expanded structure were introduced. To increase the dispersion stability, in some of the compositions, carboxymethyl cellulose was added.

3. Results and Discussions

The laboratory researches shown that a parameter which sensibly describes the fire resistance is the expansion index [6], this representing the percentage increase of protection layer thickness under the fire action in report with the initial thickness.

$$I_{\mathrm{exp}} = \frac{\Delta \mathrm{h}}{\mathrm{h_i}} \cdot 100 \qquad [\%]$$

where: I_{exp} = expansion index, Δh = difference between layer final and initial thickness; h_i = thickness of the initial layer.

Thus, thermofoaming compositions with expansion indexes, determined in laboratory, of 300-1000%, in function of the heat flux, film thickness and the substrate nature and surface geometry, were obtained. The values for the expansion index determined in laboratory are few times smaller than the ones obtained in the case of a fire.

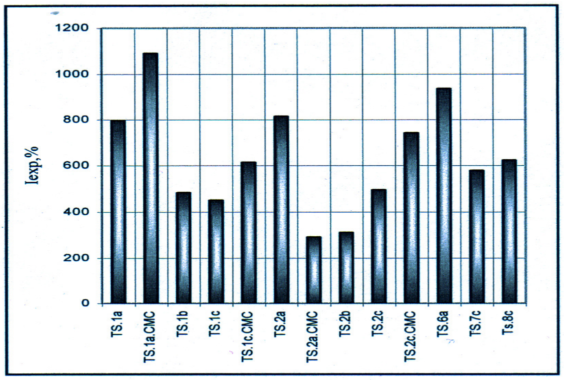

Figure 1. Comparative values for the expansion index for different compositions

In figure 1 is represented the variation of expansion indexes for different thermofoaming compositions obtained. From this figure is observed that the best results, in report with expansion index, are obtained for TS.1a.CMC, TS.2a, TS.2c.CMC and Ts.6a compositions. Taking into account the expanded layers rigidity and time stability, compositions TS.2a and TS.2c.CMC were selected for preliminary fire tests.

The high dispersed systems are characterized through thermodynamic instability, dispersed phases having the tendency to form aggregates which sediment. The use of small sized charges with controlled properties imposes important problems in regard to rheologic aspects. This is the reason why the improvement of rheologic characteristics regarding pseudo-plasticity and thixotropy, which determine the application on substrate and initial adhesion, was pursued. Analysis of rheologic properties of dispersions and settlement of optimum filler concentrations was done. The rheologic behaviour of intumescent aqueous systems was studied in collaboration with University of Bucharest – Faculty of Chemistry, using a rotation viscosimeter which develops shearing speeds, $\dot{\gamma}$, between 0.6 and $3.0 \cdot 10^4$ s^{-1}, shearing tensions, τ, between $1\text{-}10^5$Pa, and, in function of the sensor system used, can measure the apparent viscosities, η^*, in the range 1 to 10^9 mPa·s.

In the TS.2a system, containing kaolin, rheologic measures have been possible also for smaller shearing speeds, the entry on scale starting from 3 s^{-1} and extending to 1312. This is the strongest pseudo-plastic solution. The rheogram obtained at the first measurement of shearing speeds is represented in figure 2, and in figure 3 is rendered the linearization of $\eta\text{-}\dot{\gamma}$ dependency for the data presented figure 2.

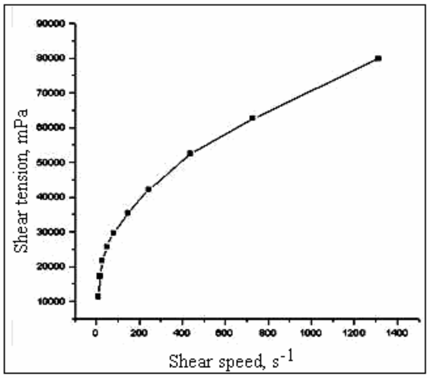

Figure 2. Rheogram of the TS.2a system obtained at increase of shearing speeds

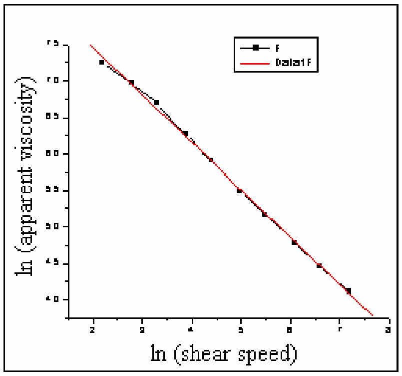

Figure 3. Linearization of $\eta\text{-}\dot{\gamma}$ dependency for the data presented figure 2 (all points)

Equation of the straight line resulting from figure 3 is:

$$\ln\eta^* = 8.7562 - 0.6504 \ln \dot{\gamma}$$

where: η^* - apparent viscosity, mPa.s; $\dot{\gamma}$ - shearing speed, s^{-1}.

The correlation coefficient has the value of 0.99915, and standard deviation is higher, 0,0473, especially due to the point of the smallest shearing speed, much more under the line. Viscosity at shearing speed zero has the value 6349.94 mPa.s. If the first two points are excluded from the figure 3, the straight line of figure 4 will be obtained, with a better correlation coefficient, of 0.99947, standard deviation of 0.0316 and expression given by the equation:

$$\ln\eta^* = 8.8423 - 0.6654 \ln \dot{\gamma}$$

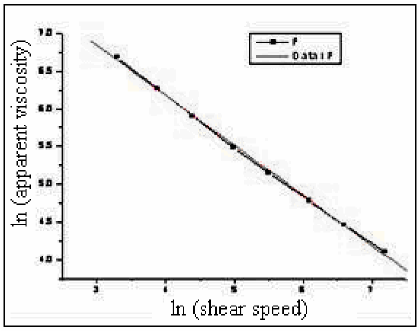

Figure 4. Linearization of apparent viscosity-shearing speed dependency
for the data of figure 2 (without the first point)

If at the TS.2c compositions, carboxymethyl cellulose (CMC) is added, TS.2c.CMC, the viscosity of the system is enhanced and this modifies the rheologic behaviour type, becoming pseudo-plastic, as it can be seen in figure 5 representing the rheogram obtained at the first increase of the shearing speeds.

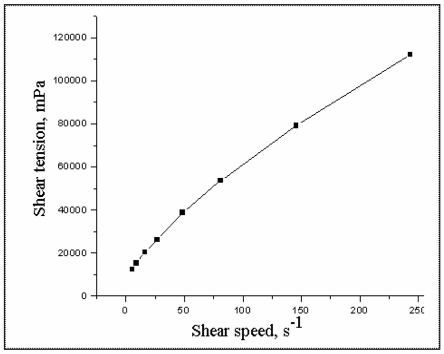

Figure 5. Rheogram obtained
at increasing shearing speeds

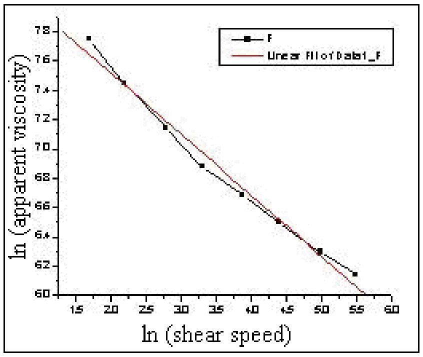

Figure 6. Linearization of the apparent
viscosity-shearing speed data from rheogram 5

The linearization of apparent viscosity data obtained from the rheogram (figure 6) lead to the straight line equation:

$$\ln \eta^* = 8.3501 - 0.4169 \ln \dot{\gamma}$$

from where is obtained η_o = 4230.60 mPa·s, close to 100 times (93.6) greater than in the absence of CMC.

The correlation coefficient has the value 0.99284, and the standard deviation -0.07265. In fact, is observed that figure 6 is constituted from two straight lines which intersect at the value corresponding to the shearing speed of 27 s^{-1}. At this shearing speed, takes place the system destructuralization, which does not continue at higher shearing speeds.

From the researches done, was observed that the introduction of kaolin in the compositions based on diacid ammonium phosphate has as effect the increase of system viscosity and pseudo-plastic character, and the introduction of carboxymethyl cellulose increases much the viscosity, transforming the ideal plastic behaviour into pseudo-plastic. These researches pursued obtaining of an increased adherence to different substrates (metal, plastic masses, concrete etc.) to eliminate the adherence primer. The use of inorganic charges with controlled concentration of surface active groups confer a series of superior properties in compared with the known intumescent compositions: high fire resistance, increased adherence to substrate and reduced gas permeability.

For fire resistant, expandable coatings, charges must have high thermal resistance, small sizes and an adequate specific weight not to hinder burning foam development. The inorganic charges performances used until now are not longer sufficient in the case of some compositions with multiple functionalities being necessary the use of inorganic charges with high specific surface, small size of particles and a controlled concentration of surface active groups. Forming the inorganic-organic networks in protection layers leads to cohesion, the rheologic response of protection film-substrate assembly having as result the improvement of adherence, mechanical properties and ageing resistance.

In composition exists a passivation system for insuring anticorrosive protection of metallic surfaces, their efficiency has being analyzed through interface studies, using the ESEM method. Characterizations at the protection coatings surface were done at nano and microscale, the results being used to settle correlation between the obtained films structure and properties.

The optimal compositions (TS.2a and TS.2c.CMC), in report with the expansion index and other selection criteria were subjected to preliminary fire tests at INCERC through a vertical oven for experimental model tests. The materials were applied on metallic poles with the I12 profile, 250 mm tall.

In figures 7 and 8 are presented some aspects during experimentations.

Figure 7. Metallic poles protected with thermofoaming materials, before testing

Figure 8. Expansion of the film during testing

The fire resistance time for both compositions has been higher than 60 minutes, the formed foam being resistant and adherent to the metallic support.

4. Conclusions

At ICEMENERG, ecological fire protection thermofoaming materials based on nonchlorinated binders and expansion agents, polyols as carbon source, ammonia phosphates and polyphosphates as acid source, mineral incombustible charges and water as the dispersion environment.

The films submitted to fire had expansion indexes determined in laboratory of 300-1000%, in function of the heat flux, film thickness, nature and geometry of the surface on which are applied. The fire resistance time determined on metallic poles was greater than 60 minutes, and the formed foam was resistant and adherent to the metallic support. The ecological fire protection thermofoaming materials obtained do not contain into composition solvents and halogenated products, do not require the use of adherence primers and have high fire resistance.

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