DEVELOPMENT OF A NEW NEUTRON SHIELDING MATERIAL, TN™ RESIN VYAL FOR TRANSPORT/STORAGE CASKS FOR RADIOACTIVE MATERIALS

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ABSTRACT

TN™ Resin Vyal, a patent pending composite, is a new neutron shielding material developed by COGEMA LOGISTICS for transport/storage casks of radioactive materials (spent fuel, reprocessed fuel,…).
This material is composed of a thermosetting resin (vinylester resin in solution of styrene) and two mineral fillers (alumine hydrate and zinc borate). Its shielding ability for neutron radiation is related to a high hydrogen content (for slowing down neutrons) and a high boron content (for absorbing neutrons). Source of hydrogen is organic matrix (resin) and alumine hydrate; source of boron is zinc borate. Atomic concentrations are equal to 5.10^{22} at/cm^3 for hydrogen and 9.10^{20} at/cm^3 for boron. Due to the flame retardant character of components, the final material has a good fire resistance (it is auto-extinguishable). Its density is equal to 1,8.

The manufacturing process of these material is easy : it consists in mixing the fillers and pouring in-situ (in cask) ; so, the curing of this composite, which leads to a three-dimensional structure, takes place at ambient temperature.

Temperature resistance of this material was evaluated by performing exposition tests of samples at different temperatures (150°C to 170°C). According to tests results, its maximal temperature of use was confirmed equal to 160°C.

TN trademark of COGEMA LOGISTICS

1- INTRODUCTION

To improve the thermal performance of the neutron shielding materials used in transport/storage casks for radioactive materials, a new material, TN™ Resin Vyal, was developed by COGEMA LOGISTICS.

This paper presents its properties (chemical, physical, thermal and mechanical), pouring process and performances (thermal resistance).

2- THE SPECIFICATION FOR THE NEW NEUTRON SHIELDING MATERIAL

COGEMA LOGISTICS has developed its own neutron shielding materials for its transport/storage casks.

The specification for new neutron shielding material is the following :

a) Chemical composition : the neutron shielding ability is directly related to hydrogen and boron contents (hydrogen to slow down neutrons and boron to absorb them). The atomic concentrations required to obtain a good shielding ability for radiation are the following :
- for hydrogen : $4.10^{22} < [H] < 5.10^{22}$ at/cm^3
- for boron : $8.10^{20} < [B] < 9.10^{20}$ at/cm^3

b) Specific gravity : density value for neutron shielding materials used for casks is around 1.8. For new neutron shielding with a similar shielding capacity, specific gravity must not be higher, to maintain a good payload for the cask.

c) Thermal expansion coefficient : values for current neutron shielding materials are between 50.10^{-6} K^{-1} and 150.10^{-6} K^{-1} (10 times higher than metals in contact like steel). The thermal expansion coefficient value for new neutron shielding material must not be higher than these values (to avoid creation of important constraints due to differential thermal expansion between metallic parts and other materials).

d) Thermal resistance : the chemical structure of neutron shielding material must not be significantly changed when exposed to high temperature over a long period. Resistance at 160°C is preferred.

e) Fire resistance : all neutron shielding materials used in casks must be self-extinguishable (burning must stop after putting out the fire), to avoid heat supply after fire. This characteristic is generally obtained by adding flame retardant fillers in the formulation.

f) Cask manufacturing process : neutron shielding material must be manufactured easily; “in-situ” pouring (directly in the cask) is a preferred process.

g) Cost : comparable to other neutron shielding materials currently used.

3- COMPOSITION AND POURING PROCESS OF TN™ RESIN VYAL

3-1 Composition of TN™ resin Vyal

TN™ resin Vyal is composed of :
- an organic matrix : vinylester resin in solution in styrene (source of hydrogen) ;
- minerals fillers : alumine hydrate (flame retardant, source of hydrogen) and zinc borate (flame retardant, source of boron).

The reticulation of vinylester resin is obtained by the addition of a catalyst (organic peroxide) to the viscous mix (matrix and mineral fillers); this addition activates, by the formation of free radicals, a reaction between double bonds of vinylester polymer and those of the vinyl group of styrene. Then, styrene is chemically bound to the vinylester matrix, leading to a rigid three-dimensional lattice; mineral fillers are dispersed in the reticulated resin structure. An accelerator is added to increase the rate of the cross-linking reaction of the vinylester resin.

This polymerization is an exothermic reaction. Two stages are observed after the addition of a catalyst : gelling of the viscous mix (characterized by a gelling time) and hardening. Gelling time depends on several parameters like the quantities of the accelerator, catalyst and temperature.

The final product obtained is a thermosetting material, insoluble and infusible.

3-2 Pouring process of TN™ resin Vyal

The TN™ resin Vyal pouring process in a transport/storage cask is fast and easy; it results from COGEMA LOGISTICS’ experience in polyester based neutron shielding materials.

The TN™ resin Vyal pouring process includes three main stages :
- weighing and mixing the different components
- degassing of the mixing under vacuum
- pouring in cask. Achievable with a viscosity around 150-200 Poises obtained at 25°C.

These operations are performed at ambient temperature.

As for neutron shielding material made of a polyester matrix, pouring can be manual or with machine (similar process).

The pouring process of TN™ resin Vyal was qualified on a mock-up to determine the parameters of the polymerization reaction. The final reticulated product is homogeneous (no decantation of fillers was observed) with a low shrinkage (0.8%).

4- PHYSICAL AND THERMAL PROPERTIES

4-1 Specific gravity

Specific gravity is equal to 1.8.

4-2 Thermal properties

The values of typical thermal properties are mentioned in table 1. Glass transition temperature, thermal expansion coefficient and specific heat were determined by differential scanning calorimetry.

glass transition temperature Tg	130°C	
thermal expansion coefficient	**T < Tg**	≅ 40.10^{-6} K^{-1}
	T> Tg	≅ 110.10^{-6} K^{-1}
specific heat (J/Kg/°C) at 160°C	1600	
thermal conductivity (W/m/K) at 150°C	≅ 0.8	

Table 1 : Thermal properties of TN™ resin Vyal

5- THERMAL RESISTANCE

The thermal resistance of TN™ resin Vyal was examined by performing exposition tests on several samples at different temperatures : 150°C, 160°C and 170°C. Two types of samples were tested : pellets (∅ = 25 mm ; thickness : 1 mm) and blocks (95 × 35 × 25 mm and 100 × 100 × 50 mm).

Similar samples made of other neutron shielding (made of polyester matrix) were also exposed simultaneously to compare their thermal resistance. The test lasted for 7 months.

Different analyses were carried out during and after tests :
- gravimetrical analysis : evolution of weight loss during temperature exposure
- micrographic observations and infrared analysis : evolution of chemical structure.

5-1 Gravimetric analysis

Figure 1 represents trends in weight loss for samples (∅ = 25 mm; thickness = 1 mm) during exposure (7 months) at 150°C, 160°C and 170°C. Trends at 150°C and 160°C for samples of polyester based material were also reported.

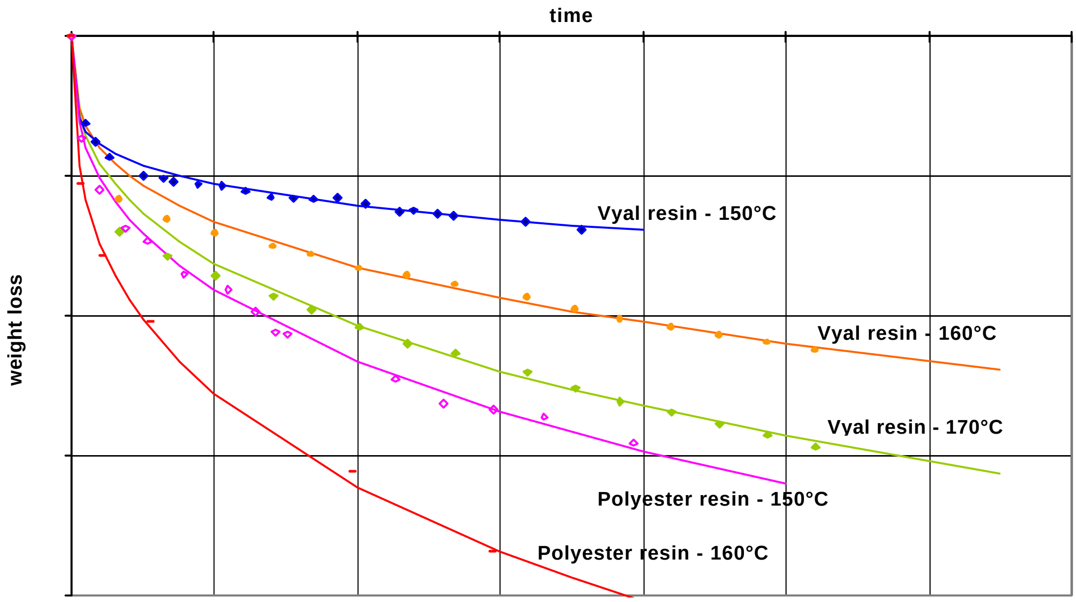

Figure 1 : Weight loss trends at 150°C, 160°C and 170°C for TN™ resin Vyal and polyester based samples (Æ = 25 mm ; thickness = 1 mm)

Curves show that weight loss of TN™ resin Vyal at 160°C is lower than weight loss of polyester based material at 150°C for the same exposure time. The weight loss kinetic of the material with a polyester matrix is greater than that of TN™ resin Vyal.
This difference can be explained by a better thermal stability of the organic matrix (the difference between two materials is the nature of the organic matrix).

According to macrographic examinations, only a few cracks were observed on TN™ resin Vyal samples exposed at 170°C for 7 months. No cracking was observed on surface of samples exposed at 150°C and 160°C.

Figure 2 represents weight loss trends during exposure (7 months) at 160°C for different TN™ resin Vyal samples. Results show that weight loss depends on surface/volume ratio : higher mass loss was observed for higher surface/volume ratio.

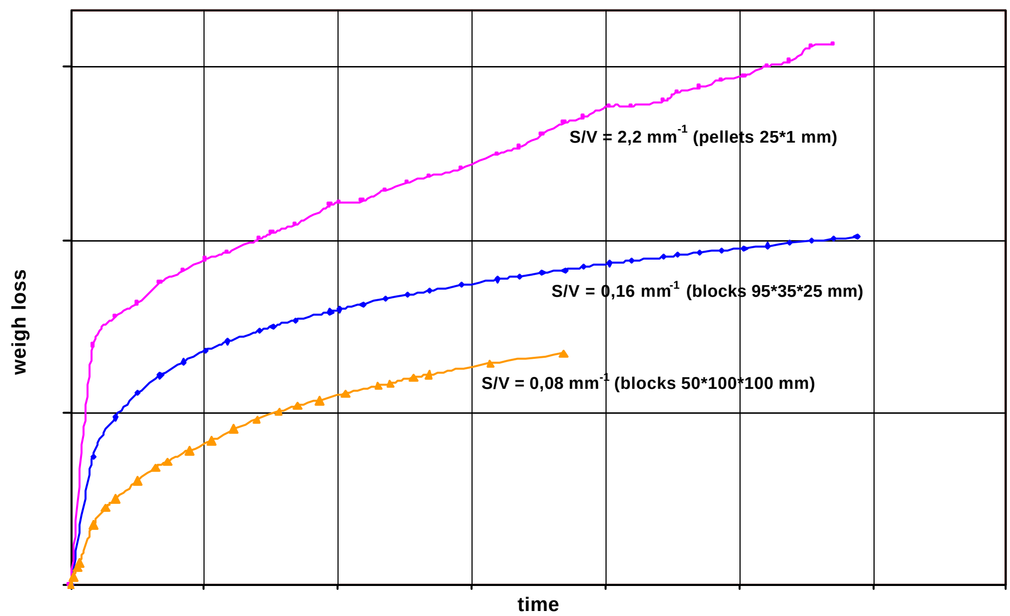

Figure 2 : Weight loss trends during exposure at 160°C for different TN™ resin Vyal samples (pellets and blocks)

5.2 Micrographic observations and infrared analysis

Micrographic analyses were carried out on a cross section of TN™ resin Vyal samples (100×100×50mm) exposed to three temperatures for different durations.
An oxided layer was observed in the vicinity of the surface ; its maximum thickness was estimated around 0.5mm. Moreover, the thickness is not related to temperature exposure and duration (this maximum value was not observed for maximum temperature and maximum exposure time).

Infrared analyses confirm that the oxidation of the matrix is superficial : an evolution of chemical structure, corresponding to the matrix oxidation, concerns only the surface ; no evolution was observed inside the samples.

6- FIRE RESISTANCE

The behaviour of TN™ resin Vyal in accident conditions must be known to quantify the efficiency loss of the neutron shielding after a fire.
Fire tests at 800°C for 30 minutes were performed on samples (∅ = 240 mm; height = 60 mm) under the following two conditions :
- flame in direct contact with resin material (sample A) ;
- with a steel plate (thickness = 1 mm) between resin material and flame (sample B).

After putting out the fire, the resin is self-extinguishable instantaneously (self-extinguishable duration : 0 second).

Two cylinder samples were taken as samples for analysis by a plasma emission spectroscopy for hydrogen and boron contents at the surface and at different depths.
Hydrogen loss was observed to a depth of 13 mm for sample A and 10 mm for sample B. An equivalent depth of burnt resin was estimated equal to 3 mm.

7- CONCLUSION

In order to meet the new customer request concerning nuclear fuel transportation and storage with higher heat power and burn-up, COGEMA LOGISTICS has developed a new neutron shielding material to increase the thermal performance of its transport/storage casks.

Compared to other neutron shielding materials developed and used by COGEMA LOGISTICS, TN™ resin Vyal presents a better thermal performance (it can be used at 160°C) with a comparable neutron shielding efficiency, similar physical (specific gravity) and thermal characteristics, a similar pouring process ("in-situ") and an equivalent cost.