

SYNTHESIS REPORT

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TITLE :

DEVELOPMENT! OF NEW MATERIALS WITH IMPROVED FIRE RESISTANCE,
REDUCED SMOKE AND TOXICITY

PROJECT

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ABSTRACT

New alternative halogen free thermoset polymers that meet processing, thermal, flammability and environmental requirements have now become necessary for mass transport applications. Based on the synergistic effects of nitrogen and phosphorus compounds, new telechelic phosphorylated crosslinkable monomers (reactive phosphine oxides, reactive phosphazenes . . .) have been synthesised as an alternative to the hazardous fire retardant systems commonly used. New formulations have been produced and selected on the basis of simple thermomechanical characteristics, fire performance, predictive toxicity assessment and parallel fundamental investigations on their degradation mechanisms.

They have been used for further fibre impregnation of composite test samples and demonstration pieces. This document presents the general organisation of the project and the main characteristics (fire, thermomechanical, mechanical, degradation) of the novel fire retarded materials developed, which show (for composites) an improvement from 40% to 70% of fire properties without loss of thermal and mechanical behaviour.

I-GENERAL

L 1- INTRODUCTION

The increasing use of organic materials in transport vehicles and in the construction industry means that fire as a hazard to life and property has increased in importance. Recent events have highlighted the need to improve fire resistance. This clearly entails a more comprehensive appraisal of all aspects of the combustion of organic materials and, more importantly, the ways of preventing it. Reductions in the propensity of organic materials to ignite or emit dense and/or toxic fumes are equally important.

Ignition of organic materials occurs either spontaneously or from an external source, if the concentration of volatile combustible products evolved by thermal/thermal oxidative degradation of the polymer is within the flammability limits.

A self sustained combustion cycle is then triggered. TMs is driven by the heat of the flame promoting the pyrolysis of the polymer. The process will continue as long as the heat transmitted to the polymer is sufficient to keep its rate of thermal degradation above the level required to feed the flame, otherwise it will extinguish.

The self sustained combustion cycle occurs in the condensed and gas phases.

In order to extinguish the flame by depressing the rate of chemical and/or physical processes taking place in one or both phases, organic materials currently contain a variety of additives that may act as fire retardants.

Early developments in this field, mostly based on an empirical approach, led to the recognition of fire retardant actions of compounds containing one or more of the following atoms: Cl, Br, P, N, B, Sb, Al, Mg. Halogen-based systems combined with some other additives (e.g. Sb_2O_3) are among the most widely used fire retardants, in particular for composite organic matrices such as phenolic, epoxide or bismaleimide resins.

However on burning they generally evolve halogen acids and metal halides; the proven efficiency of these products has to be balanced against this formation of noxious, corrosive and obscuring fumes.

Moreover, it has been recently pointed out that, some currently used brominated fire retardants may form extremely toxic brominated dibenzodioxins and dibenzofurans. Some questions about the toxic potency of antimony trioxide has led to objections concerning its safe handling and use.

1.2 - OBJECTIVES

The **main** objectives of this project were to develop **new materials with improved fire resistance, reduced smoke and toxic gas emissions for structural and/or furnishing applications.**

The research has involved three main aspects:

1- Synthesizing and supplying new halogen-free telechelic or crosslinkable phosphorus containing monomers such as amino or alcohol modified phosphine oxide and reactive phosphazenes as an alternative to the hazardous fire retardant systems commonly used. This has led to an optimisation of the fire behaviour (fire, smoke, toxicity . . .) of current thermoset formulations by incorporation of the so developed telechelic phosphorylated flame retardant monomers.

2- Broadening fundamental knowledge of the self-extinguishing mechanisms and the thermal behaviour of the developed materials considering the composition of the polymer and the different fire parameters and scenarios (volume, oxygen or air fluxes, temperature, . . .).

3- Evaluation of (fire, smoke, toxicity, corrosivity, thermo-mechanical properties, chemical structures of the cured network . . .) the neat resins and of the resulting composites in order to define their potential use with regard to fire safety and applicability.

At the start of this research, the main objectives envisaged for the development of these new fire retarded materials were as follows,

- **high thermo-mechanical properties of the materials** : comparable with or better than the current thermoset systems with regard to their potential application. **Seven types** of formulations were produced ; corresponding prepregs should present a good conformability and have : i) to **accept distortions to allow the lay-up of non developable pieces**, ii) **an acceptable adhesion on itself and on the tools at room temperature**, iii) **15 days minimum shelf-life at room temperature**,

improved fire resistance : the glass transition (wet) of the developed materials should exceed if possible **160°C** and the heat release peak (OSU test) of composites should be below **50 kW/m²** which represents ~ **40%0** of decrease compared with the current average values,

low toxicity level of the fumes emitted on burning and of the basic formulations achieved by a **suppression of the halogen and other suspected toxic compounds in the matrices.**

The originality of this work stems from the production of a range of novel phosphorus containing resins, whose structure and composition can be tailored to allow systematic optimisation of fire retardancy and thermomechanical properties.

1.3 - ECONOMIC POTENTIAL, INDUSTRIAL AND ENVIRONMENTAL BENEFITS

The proposed research was aimed to develop new materials [**resins and composites**] which combine **improved fire resistance, reduced smoke and toxicity, and meet suitable processing, environmental and thermo-mechanical characteristics for structural and/or furnishing applications.**

This has been achieved by using a dualistic basic and industrial approach on the binary system fire-retardant/matrix.

The main expected interest of this research is to provide in the near future a list of possible **substitutes of the common hazardous fire retardants to be used in current thermoset polymers (epoxies, bismaleimides, cyanates, . . .) to improve their fire resistance.**

Mainly based on the phosphorus/nitrogen synergy, these new telechelic fire retarded materials will then allow :

- **improvement of the levels of thermo-mechanical characteristics because of direct linkages with the network**,

a **decrease in their toxic and ecotoxic potency** by suppressing halogens and some other toxic additives in the matrices,

anticipation of possible relevant regulations,

a contribution to an increase in the hope of survival in case of fire and the containment of the fire damage in order to preserve most of the equipment.

- * Publications estimate that the market of composites is continuously increasing by - **25%/year** and will represent a turn over of 7610 **million US\$** in 1995.

Evolution of the market of composites in millions \$

	1990	1995	Annual growth rate %
USA	1650	3650	19
JAPAN	650	1650	23
EUROPE	610	1700	21
OTHERS	80	210	26
TOTAL	3.000	7610	21

The **epoxide matrices** represent **87%** of the **composite resins**, and **phenolics** 9%. This study is targeted at interior fittings, (i.e., products that are used as liners in the aircraft fuselages and the furnitures inside the transport vehicles (galleys, storage bins, . .)). This application represents 16% of the **total composite business**.

The improved products that will be brought to the market after this study will affect 25% of the above business, which suggests that the market share of these products will represent 4% of the global composites market. That means in the year 1995:

(M = Millions)

'USA	155
JAPAN	74
EUROPE	6S
<u>OTHERS</u>	<u>8</u>
Total	305 M\$

Considering that the developed materials could find applications in many sectors of industry such as automotive, aerospace, railways, building, electronics, . . . the relevant share of the market is then increased.

- * Composites market figures obtained from Aérospatiale.

1.4 - MEANS USED TO ACHIEVE THE OBJECTIVES

The means to achieve the objectives of this project were mainly based on:

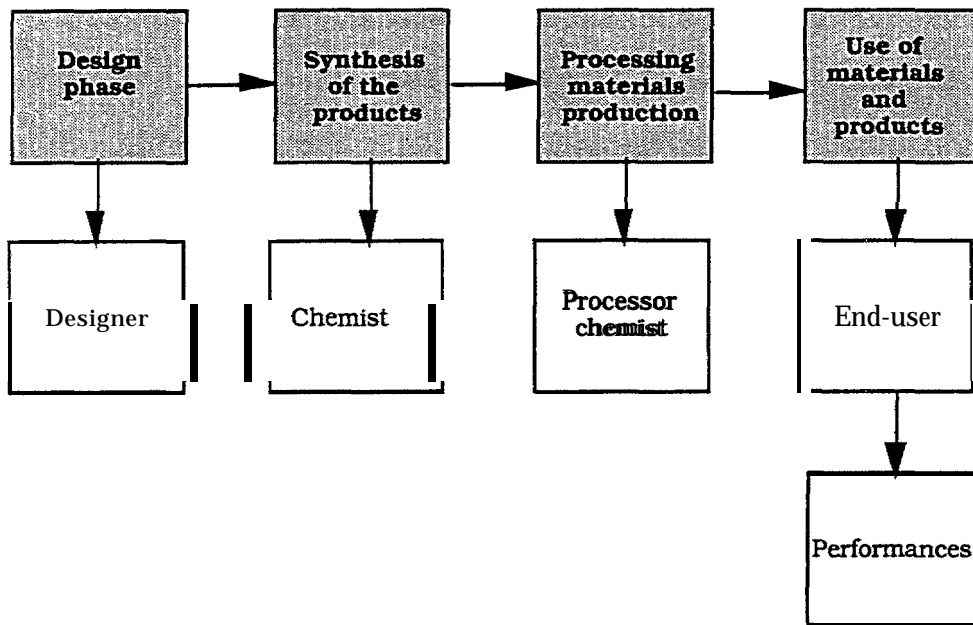
- the **existence of an original management scheme and of the organisation of the project**,
- the creation of a consortium,

which both allow respect for the subsidiarity principle of competence and permit each company involved to implement the corresponding and necessary technical means and manpower with a continuous feed-back to all the partners.

1.4.1- Existence of an original management scheme and organisation of the project

As the development of new products involves not only the design and synthesis phase but has also to consider the processing potency, the possible handling of the products (toxicity), the fate of the products along their life-cycle, including the disposal and destruction phase, the structure of the project has been organised taking all of these main phases into account.

Basic life cycle of a product



1.4.2- **Creation of a consortium**

To investigate and exploit this new concept of new fire retardants, a consortium has been created by AEROSPATIALE, under the authority or EC-DGXII. The goal is to develop new materials (components → resins → prepregs → composites) which comply with aerospace requirements as well as current and future health and safety regulations.

Following consideration of the development and evaluation of new fire retardant materials, the solution may lie in using these materials in aeronautical construction and even in **other** industries, e.g. railway applications.

Partners involved are, in alphabetical order:

AEROSPATIALE : Aerospace constructor,

BRUNET-SICAP : Composite parts and assemblies manufacturer,

Minnesota 3M Research Ltd, Harlow : Synthesis, characterization and formulation of new-products.

SNPE (Société Nationale des Poudres et Explosifs) : synthesis, characterization, formulation and prepregging of new materials,

University of DUBLIN : Toxicity of chemicals and materials,

University of TORINO : Fire retardancy mechanisms.

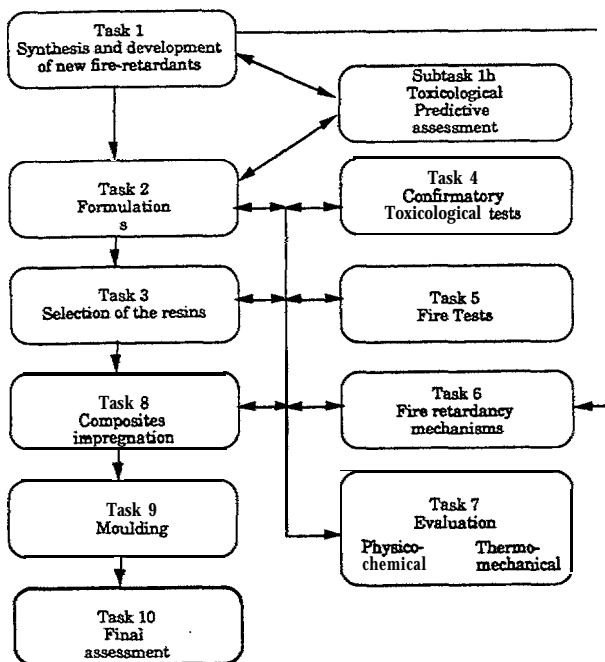
The tasks devoted to each partner and the organisation of the research are described in Part II (scientific and technical aspects of the project).

H - SCIENTIFIC AND TECHNICAL DESCRIPTION

II.1 - RESEARCH PROGRAMME [ORGANISATION OF THE STUDY]

The progression of the work task by task together with the interaction between the tasks is laid out in tabular form in the flow chart, page 6.

Research framework



111.1 - SYNTHESIS OF NEW FIRE RETARDANTS

Three chemicals (or family of) have been developed as new fire retardants:

- amino phenyl phosphine oxide S001 (SNPE),
- phenyl phosphine cyanate oxide S003 (SNPE and 3M),
- phosphazenes (3M) - Example: M007.

More than 20 novel phosphorylated flame retardant crosslinkable monomers have been prepared. Two based upon phosphine oxide and phosphazene chemistries were scaled up to more than 10 kg as a result of the input from tasks 2, 1 h, 4,5,6 and 7.

These dual telechelic materials act both as flame retardant and curative.

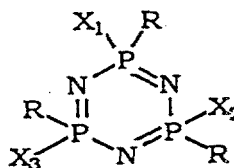
Ease and cost of synthesis were taken into account in choosing promising candidates for further study. Limited formulation was then performed in epoxy resin systems to determine thermomechanical and flammability properties and also the efficiency of these flame retardant materials as curatives.

General **synthetic targets** were of the form:

- (1) di/tri amino phosphazenes
- (2) di/tri hydroxy phosphazenes

Examples:

(ex: M007)



X₁, X₂, (X₃) = NH₂, OH

The main steps for the development of new materials are:

- synthesis of fire retardants → step 1,
- preparation of formulations and selection → step 2,
- manufacturing of prepregs → step 3,
- preparation of composite samples [and aeronautical assemblies] → step 4.

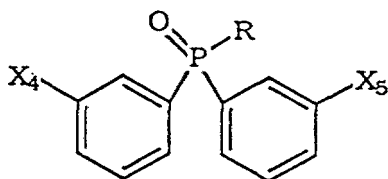
For each step, all the necessary characterizations and also fire retardancy studies and toxicity assessments were performed for each product developed.

III - TECHNICAL RESULTS

The summary of the work done and related technical detail is presented according to the 4 main steps described below.

(3) Phosphine oxide derivatives

(ex: S001)



X₄, X₅, = linking moiety

On the contrary, cyanate phosphine oxide derivative, S003 presents a difficult and hazardous synthesis, is very expensive and does not improve fire properties.

300 g of S003 were synthesised and characterized without scale-up and any further development.

The selected M007 and S001 fire retardants were fully characterized (thermal, physico chemical and toxicity assessment).

III.2 - FORMULATIONS

III.2.1 - Optimisation and selection

Starting from the two selected fire retardants, different formulations were prepared in two main chemical families: epoxies and bismaleimides (BMI) currently used as resins of composite materials.

The general formulation is :

base [Epoxies (1 or 2) or BMI],

hardeners (stoichiometric ratio of reactive functions/epoxy or BMI functional groups):

- "typical hardener",
- and fire retardant hardener (M007 or S001).

for toughened systems, addition of high performance (thermal, mechanical) plasticizer (TP: thermoplastic).

Around 50 preliminary formulation studies (toughened and untoughened) epoxies, BMI, cyanates all containing phosphorylated crosslinking monomers resulted, after screening tests in the choice of 3 phosphorylated materials for scale-up, in depth formulation and evaluation in 6 classes.

The 6 preliminary optimised formulations were:

- F1 : Untoughened Epoxy /S001 (phosphine oxide).
- F2 : Toughened Epoxy/S001 (phosphine oxide).
- F3 : Untoughened BMI/S001 (phosphine oxide).
- F4 : Untoughened Cyanate/S003 (phosphine oxide cyanate).
- F6 : Untoughened Epoxy /M007 (phosphazene).
- F7 : Toughened Epoxy /Moo7 (phosphazene).

A complete screening including fire, thermal, mechanical and toxicological tests was performed.

To obtain the best balance between fire and mechanical behaviour, the three following formulations have been selected and scaled-up:

- F2 : toughened phosphine oxide based epoxy,
- F3 : phosphine oxide based BMI,
- F7 : toughened phosphazene based epoxy.

III.2.2 - Characteristics of the **three selected formulations**

The different tests (or studies and assessments) are described below

a) Thermal and thermomechanical tests

DSC to follow the cure rate/exotherm,

DMA to determine dry T_G and wet T_G (after aging in water): wet $T_G \approx 150-160^\circ\text{C}$, a little bit lower for pure resins than the objective target $> 160^\circ\text{C}$.

b) Fire tests:

Cone calorimetry to measure ignitability, heat release rate (RHR), smoke and toxic gas production and used also for the initial screening, on resins.

OSU (OHIO STATE UNIVERSITY) testing has also been carried out for aeronautical application: determination of the heat release peak HR max (kW/m^2) and the integrated value for two minutes HR2 min ($\text{kW}\cdot\text{min}/\text{m}^2$) according to FAR 25853 specification.

c) Toxicological predictive assessment and confirmatory toxicological tests

Of 26 candidates and 18 formulations, the chemicals have been examined for their potential toxicity using computerized prediction (TOPKAT). 11 parameters of toxicity or ecotoxicity have been examined.

Only 4 chemicals present indications of some predicted mutagenic or carcinogenic potential (phosphine oxides and epoxy).

Confirmatory tests with the two methods MICROTOXTM and MUTATOXTM (metabolic inhibition and genotoxicity) show that only two chemicals (BMI basis) presents genotoxic risk.

d) Mechanism of fire retardant action

1. Phosphorylated hardeners increase char formation thus reducing flammable volatile compounds evolved from thermal degradation of the resin.
2. The char is thermally stable and shows a foam like structure (intumescent) which provides an effective thermally insulating shield to the resin.
3. The fire retardant action of intumescent char from S001 is lowered by its thermal oxidation.
4. The chemical mechanism of thermal degradation of epoxy and BMI resins and of the charring processes is understood and can serve for future adaptation of the phosphorylated curing agents to other thermosets.

e) Mechanical test

Only K_{1C} measurements were carried out on cured pure resin to determine the toughness. Toughened epoxies systems are close to typical aeronautical systems $K_{1C} \sim 0.5 \text{ MPa}\cdot\text{m}^{1/2}$ and very much higher than corresponding untoughened epoxies F1 and F6, untoughened BMI is more brittle ($K_{1C} \approx 0.25$).

f) Physicochemical characterization

All the formulations and their individual components were extensively characterized (FT-IR, HPLC, GPC, MS, ^1H NMR, ^{13}C NMR, MS). The kinetics of polymerisation were followed by FT-IR and DSC and show a complete conversion before the end of the cure cycle.

III.2.3 - Deliverables

For the three selected formulations F2, F3, F7, scale-up to 25 kg for prepregging was performed in each case:

III.3 - PREPREGS

Three prepregs have been developed by impregnation of each resin (F2, F3, F7) on UD carbon fiber:

in a first step, at the laboratory scale to determine the parameters necessary for the ability to prepregging,

in a second step, scaled up to approximately 100 m², in order to provide quantities required for:

- composite plates and pieces preparation (-80 m²),
- prepreg samples dispatched between all the partners for further characterizations.

111.3.1- Optimisation

Optimisation has been achieved by measuring and/or checking the following parameters:

- viscosity, shelf-life and tack,
- definition of the cured cycle and measurement of different parameters, including JLSS as mechanical test.

III.3.2 - Scale-up and deliverables

Approxirnatively 100 m² of each formulation were prepared according to the optimised cured cycles and fully characterized as shown in table I.

Table I: Supplied prepregs

Formulation	F2	F3	F7
Fiber	T300 12K 50B	T300 12K SOB	T300 12K 50B
Quantity (m ²)	91.8	80.4	121.5
Length (mm)	300	300	300
Fiber content (g/m ²)	147-148	148	148
Resin content (% by weight)	36-37	36-38	35-36
Prepreg weight (g/m ²)	229-235	123'-240	228-229
Volatiles (%)	<1	<1	<1
Shelf-life	>14 days	>14 days	>14 days

III.3.3 - Characterization of the prepregs

Most of the characterization has been reported earlier.

An additional physiochemical characterization has been carried out to determine (by chromatographic methods: HPLC, GPC) the degree of advancement of polymerisation during prepregging, which shows that the "B stage" is:

very important for F2 (very reactive system),

medium for F7,

low for the BMI F3 (but with consumption of BAMPO).

III.4 - COMPOSITE MATERIALS

Two forms of composite were prepared:

plates (3 kinds of layerings) to assess different properties (mechanical, fire, thermal, physical) and to compare with current materials,

moulding of real aerospace pieces as a demonstration test.

III.4.1 - Reparation of composite samples for tests

BRUNET-SICAP has prepared 23 plates which were cut by AEROSPATIALE to prepare the test samples. Additional reference test samples (epoxies, phenolics) have been also prepared.

III.4.2 - Physical characterization

All the types of composites (9: 3 resins x 3 lyings) were physically characterized:

- by measurement of the density and the fiber content,
- by micrographic observations (x 20 to x 200) they show in some places an important porosity inside the material.

III.4.3 - Thermal and thermomechanical characterization

The degree of polymerisation observed by DSC shows a full polymerisation without residual enthalpy.

Dry T_G and wet T_G (after aging 500 h - 70°C - 95% HR) have been determined by DMA.

Wet T_G decreases by approximately to 30°C for epoxies and 23°C for BMI systems.

The wet T_G values reaches the Objective, i.e., wet T_G - 160- 170°C except for F2 which has a slightly lower value (but is acceptable).

III.4.4 - Fire tests

OSU, BUNSEN flammability, NBS, Torch, Cone calorimeter and LOL.

a) OSU [OHIO STATE UNIVERSITY] tests: (according FAR 25 and JAR 25 specification)

The main values of heat release HR max and HR 2 min lead to the following observations:

- The three developed composites are in accordance with the specifications: HR and HR 2 min < 65 kW/m².
 - Compared with the reference non fire retardant epoxy an important decrease of HR is observed:
 - ~ 40% for epoxy systems,
 - - 60% for BMI systems.
 - The values are close to the best phenolic system (V260) used in aerospace furnishing.
 - The weight loss has the same magnitude as the epoxy reference, but time of HR max [- 2 min] is twice as long.
- b) BUNSEN flammability tests (according to FAR 25 and JAR 25 specifications)

All the BUNSEN flammability values (flame extinction and length "of bum) fully comply with the specification and are very close together (F2, F3 and F7).

Compared with the epoxy reference an improvement of 100% is obtained.

c) NBS (Nationale Bureau of Standard): smoke and toxicity (according FAR 25, JAR 25 and ATS 1000).

All the tests are in accordance with the specification : - smoke density and gases evolved (CO, NOx) are at the level of the epoxy reference, except for the BMI system which shows better values.

No halogenated fumes are emitted during burnig

d) Torch

Burnthrough of panels with a kerosene torch.

h-radiance : 1 19kw/m²-T°C=1 120°C

No burnthrough was observed after 15 minutes of exposure to the kerosene torch for any material (2 mm thick samples).

e) Additional test: cone calorimeter

This method (close to OSU and NBS) was applied to the 3 materials, the epoxy reference, and other references (fire retardant epoxy and phenolics systems).

- HR cone values are ranked in the same way as the OSU HR values.
- Comparison with the epoxy reference shows an improvement of ~ 30% for epoxies and ~ 50% for BMI systems.

f) Additional test : LOI (Limit Oxygen Index)

This method gives the same ranking for the three formulations as for the previous methods and shows that the orientations of the fibers has a great effect on the results (horizontal >>-vertical).

In conclusion, the newly developed composites show an improvement for all the fire characteristics and especially in the case of heat release values (HR) a decrease of: ~

- 40-50 % for epoxy systems (F2, F7),
- 65-75 % for the BMI system (F3),

compared with "typical" epoxy reference systems. All the values are in accordance with the specifications.

HR values are comparable with the best phenolic systems currently used in aerospace furnishing applications,

Our main objective, i.e., improvement of HR at least of 4096 is reached.

III.4.5 - Mechanical tests

The following mechanical properties were tested on the three developed composite materials:

a) ILSS : Interlaminar shear strength

Measurements at:

Five different temperatures 20, 70, 120, 150 and - 55°C without aging,

Three different temperatures (20, 70 and 120°C) with wet aging (1 000 h, 70°C, 95% HR),

Room temperature after MEC immersion.

The ILSS values of the 3 materials are greater than the reference epoxy and the specifications (except for F2, which has a slightly lower value).

The decrease $\Delta/(20^\circ\text{C ref})$ of ILSS at different temperatures or conditions are equivalent or better than the reference.

Water and MEC uptake were also determined at the end of the aging, water uptakes are ranked as follows:

F2 < F3 < F7
(0.35%) (0.45%) O. WA)

and MEC uptake is very small, (\approx 0.02%).

b) Tensile and oDen hole tensile

The values including the "hole coefficient" have the same magnitude as for the epoxy reference, even slightly better.

c) 3Doint bending

Same observation as for tensile tests.

d) Compression

The compression values of the new formulations are good, better than the reference material and the specification values.

e) CAI

Samples were impacted at eight different energies from 6 to 30 Joules, examined by C-Scan (NDC) and CAI was performed.

The impact behaviour of the new formulations is good, generally better than reference 914.

Delaminated area and impact depth vs energy are better, CAI is close to the reference.

Conclusion on mechanical properties:

The test values fully comply with the specification and the reference epoxy, with a slight improvement in some cases. The newly developed materials have good mechanical properties, above the level of the performance required for aerospace applications.

III.4.6 - Toxicity assessment on composites

Difficulties have appeared due to the insolubility on these materials. Nevertheless, according to the very sensitive methods applied and the negative results on components, it can be estimated that the materials present no or very low toxicity.

III.4.7 - Fire retardancy mechanisms on composites

Thermal decomposition:

Char yield is more than 80% under nitrogen and 70% under air. The presence of carbon fibers moderates the promoting effect of charring.

LOI tests (paragraph III.4.4) show that the orientation of fibers have a great importance (high LOI value for horizontal position).

Linear pyrolysis confirms a noticeable deterioration of the intumescence due to the presence of carbon fibers.

III.4.8 - Moulding of real pieces

The work of this programme was completed by the manufacture of representative workplaces for the aeronautic sector, which represents a demonstration of the developed materials.

The manufactured piece, is a rear lateral engine hood for the ATR 42-72 planes, currently manufactured in typical epoxy/carbon tissue material.

Three pieces have been built with the agreement of AEROSPATIALE, starting from the 3 prepregs F2, F3 and F7.

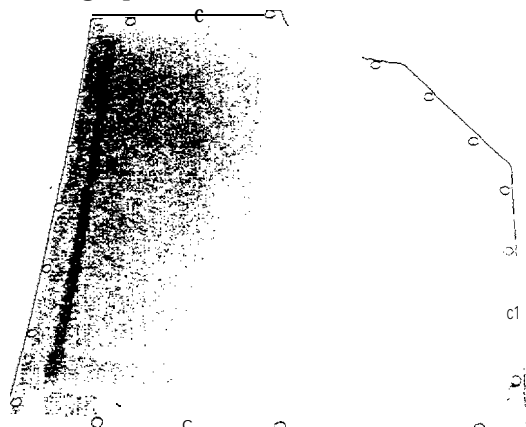
The appearance of the workplaces are satisfactory. An ultrasonic non destructive control (C-Scan Jet), together with other methods such as manual US, radiography and tape test have been performed at AEROSPATIALE.

The quality of the core of the pieces is acceptable, especially good adherence at the interface between honeycomb and composite.

The homogeneity and porosity are good for epoxy pieces, but not for the BMI piece (it seems that the cure cycle, with high temperatures, should be optimized for this resin in industrial conditions).

In summary, as a demonstration, three representative workplaces have been manufactured with the newly developed materials. A good quality has been obtained, confirmed by ultrasonic NDC.

Photograph of lateral hood below.



V - CONCLUSION A N D ACKNOWLEDGEMENTS

The main targets of this three year research based on a new approach to fire-retardant materials have been successfully reached and have led to the preparation of new materials with improved fire resistance, low toxicity and without loss of mechanical and thermal properties.

A) Four main steps involved in the research have been carried out:

1 - Synthesis and supplying of new halogen free telechelic "or crosslinkable phosphorus containing monomers: amino-phosphine oxide (BAMPO) and several functionalised phosphazenes among them the product BRITE MO07 has been selected because of their particular performances. A scale up to 10 kg (MO07) to 50 kg (BAMPO) has been performed without noticeable difficulties and at a moderate cost.

2 - Preparation of 7 formulations based of the synthesised products in association of current epoxy and bismaleimide (BMI) systems, including other hardeners and in some cases a plasticiser (thermoplastic) to obtained toughened systems.

After assessment three formulations have been selected:

- F2: Toughened Epoxy/BAMPO,
- F3: Untoughened BMI/BAMPO,
- F7: Toughened Epoxy/Phosphazene.

The assessment of fire, thermal and mechanical (K 1 C) properties of the resins has shown acceptable characteristics.

3 - Impregnation of these formulations with carbon fiber in order to obtain 100 m² of prepreg for each of them, characterization and cure cycle have been defined and optimised.

4 - Preparation of three composite materials for final assessment of all the characteristics and demonstration.

Fire properties assessed by OSU, NBS, BUNSEN, Torch, Cone, LOI tests appear to be very good, especially for the heat release HR [the most important characteristic] ; it is noticed:

- An improvement of 40-50 % for epoxy system and 65-75 % for BMI system, compared with a typical non fire retardanced system (914).
- HR values close to one of the best (fire behaviour) aerospace phenolic systems (V260).
- HR values in full compliance with the specifications.
- No release of major halogenated toxicants and decrease of fire properties.
- No burnthrough by kerosene torch on 2 mm thick samples.

All the other fire properties show similar levels and improvements.

Thermal and mechanical properties obtained are comparable with (or a little higher) than those obtained with current non fire retardant materials, no loss of mechanical behaviour has been observed with fire retardants.

Real Aerospace assemblies, rear lateral engine hoods for ATR 42-72. have been manufactured for each formulation as a demonstration and a further control shows a satisfactory quality.

B) Parallel to these different steps of the work, from synthesis of molecules to manufacture of demonstration pieces in composite materials with enhanced fire properties, basic research has been carried out on:

1 - Broadening of fundamental knowledge of self-extinguishing mechanisms and thermal behaviour of the developed materials.

2 - Assessment of the toxicity of the different materials, which finally show no (or very low) toxicity and no ecotoxicity.

In summary, new materials based on phosphorus containing telechelic molecules have been successfully developed and allow the formulation to reach an increase of 40% to 60% of the fire retardant properties with conservation of mechanical and thermal behaviour.

The originality of this new concept of reactive fire retardant is undoubtedly the main reason for this behaviour since the fire retardant molecules directly contribute to the cohesion of the network by cross linking.

This could still lead to major and further development and improvement by using this new concept in acting not only on modified hardeners but also on the basic matrices and other necessary additives → optimisation of the processing parameters could be now expected to produce fire-retardant formulations capable of RTM technology.

This further development will produce a major improvement in security for transport vehicles, in allowing for the first time the replacement of current phenolic systems by new improved systems with higher performance packages,

The present work illustrates the potential of the 13 RITE-EURAM concept in supporting the integration of multiple inputs from industrial and academic institutions. In particular this project provides evidence of success in the development of new and novel flame retardant aerospace materials.

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