AMMONIUM POLYPHOSPHATES AND INTUMESCENT COATINGS IN STRUCTURAL STEEL FIRE PROTECTION

KEYWORDS: Intumescent coatings, Steel protection, Ammonium Polyphosphate

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1- INTRODUCTION TO REACTIVE COATINGS

Passive fire protection, as defined by the Passive Fire Protection Federation, is the primary measure integrated within the layout and structure of a building to provide inherent fire safety and protection against fire, heat and smoke hazard.

Passive fire protection ultimate target is to save people life, this goal is pursued taking measures in all aspect of buildings and constructions fire safety with the specific aim of gaining time, either to control the fire or to evacuate the building: time is of essence in any fire situation, Reactive Coatings primary rating is time, which is delay for structures to reach a given temperature in a fire situation.

Reactive coatings also called Intumescent Coatings, are a fundamental tool for Fire Safety, together with Intumescent products like seals and mastics used to plug penetration gaps they are the basic elements utilised in buildings Passive fire protection: not only they retard drastically fire propagation, the flame retardant and smoke stopping capabilities of these components also enable rescue and emergency services to undertake their jobs in a more controlled environment.

Finally, damage to the building, contents and surroundings by flames or smoke may be significantly reduced.

2 HOW REACTIVE COATINGS WORK

Intumescence is the result of a sequential chemical reaction between several chemical products activated by the heat of flames during the fire. Intumescent products are those which expand (or intumesce) to several times their original size when activated by high temperatures.

The final result of the chemical reaction is the development of insulating foam that protects the material from fire and reduces the smoke and the heat transmission.

The chemical reaction is based on three components. A source of phosphoric acid, normally Ammonium polyphosphate (crystal phase II) is the catalyst agent, an organic compound with reactive OH groups that will turn into coal by the action of the phosphoric acid (normally pentaerythritol and dipentaerythritol) is the char promoter and an inert source of gas, normally melamine is the gas generator agent.

Intumescence steps

At high temperatures, APPII decomposes into polyphosphoric acid. The polyphosphoric acid reacts with the polyalcohol forming an ester. Afterwards the ester will dehydrate till the formation of a molten char. At the same time, Melamine decomposes releasing inert gases that expand the molten char, finally that char becomes a solid foam layer that act as a barrier isolating the materials from the fire heat transmission and reducing the smoke emission. See below Figure 1 (left side wood protected with a thin layer of intumescent coating, right side intumescence after flame exposure).

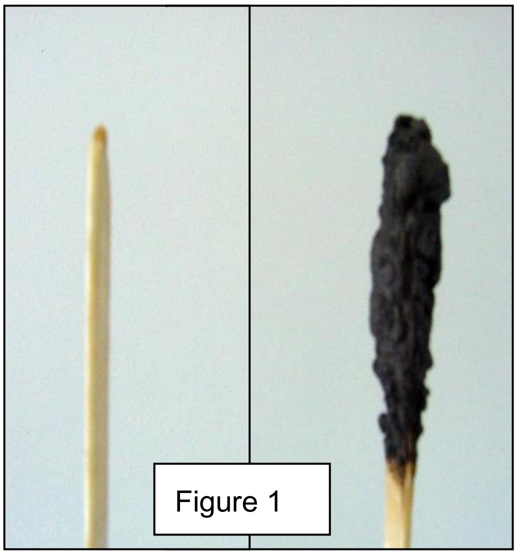

Figure 1

Fire protection for steel structures

Structural steel fire protection consists of the use of products or elements that will improve the heat stability of that structure. The fire stability of a structural element is defined as the time (in minutes), measured from the beginning of the fire, till the loss of the bearing ability of the structural elements which for steel is around 500-550º C.

Intumescent/Reactive coatings are a very effective mean to increase the fire stability of structural steel. Compared with other systems, Intumescent reactive coatings are very easy to apply, the coating thickness doesn't modify the shape and the dimensions of the structure, for this reason they can be used when the bearing elements remains in sight and are integral part of the architects efforts to combine style and efficiency.

Below on the left end of this picture, you can see a steel plate coated with 900 microns of Intumescent coating, these photographs are taken while the plate is exposed to heat in a testing furnace, the black char expand gradually and when solid turns into white color while the test proceed, which means that the organic components have been totally depleted by oxidation. The test have been terminated when the steel plate reached 500 deg C (Figure 2)

Figure 2

Fire stability of a structural element protected with reactive coating is rated in minutes.

The stability is measured using standard methods (for example in Europe, EN 13381-8 or BS475 Parts 20-21) carried out in accredited testing Laboratories. The Laboratory run tests according to the related standard and issue a report for the Coating tested, with tables and graphics, where they detail the necessary Dry Film Thickness - DFT required for a given set of steel profiles to protect the structure for 30, 60, 90 or 120 minutes.

The manufacturer of the intumescent coating must provide the paint together with the test certificate: the certificate is the key document that confirms at which DFT the paint performs in line with the Fire protection requirements for each specific building.

<u>Fire Resistance Standard Summary, EN 13381-8</u>

An important thing to explain before starting with the summary of the standard is the shape factor concept. Shape factor is a number obtained after the division of the steel perimeter exposed to fire -P- by the surface of the transversal section of the steel profile -A-.

Shape Factor (Hp/A)= P/A .The result is expressed in m^{-1}
The higher the shape factor, the higher thickness should be applied to get the same protection against fire.
Big steel profiles have lower shape factor values than small ones.

The test is made with steel profiles (16 total, beams and columns) sometimes loaded with different shape factors, dry paint thickness

The steel profiles are exposed to an ideal fire according to the ISO 834-8:2002 curve (temperature vs. time). The Cellulosic curve, also known as the "A" category fire curve, is the least intense of the fire curves and covers the basic scenario of a fire of general combustible items such as the furniture and contents of a building and its materials of construction. See Figure 3.

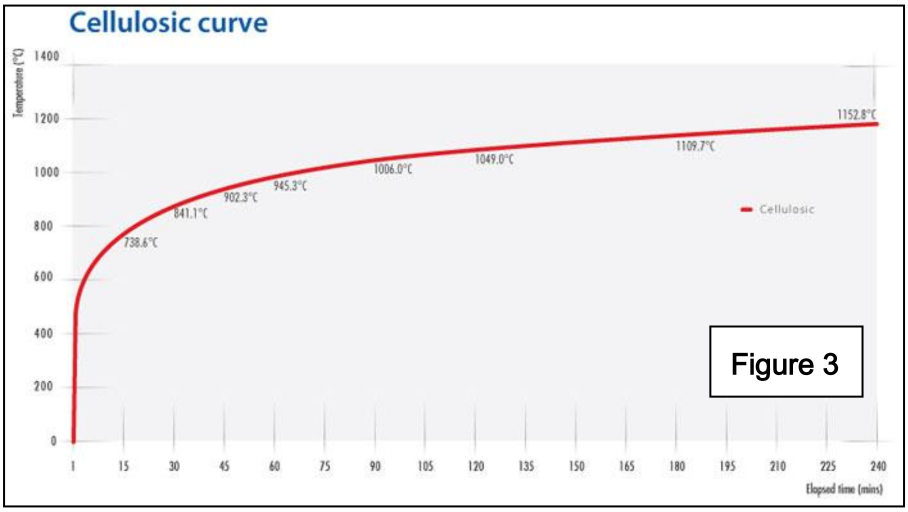

Figure 3

The results of the test are recorded using thermocouples fixed to the steel. By means of the mathematical treatment of the data, tables and graphics are obtained (interpolation). These tables and graphics –with values of dry film thickness, shape factor and fire stability- allow us to get results for other steel profiles not tested in the experiment (see attached table 1 -example for 60 minutes-).

Table 1

I-Section Columns 60 minutes									
Section Factor up to m^{-1}	Thickness (mm) required for a Design Temperature of								
	350ºC	400ºC	450ºC	500ºC	550ºC	600ºC	650ºC	700ºC	750ºC
70									
75									
80									
85									
90									
95									
100									
105									
110									
115									
...									
...									
...									
...									
350									
355									
360									
365									
370									

3- EUROPEAN STANDARDS AND REGULATIONS

Reactive coatings for structural steel fire protection are tested for resistance to fire according EN 13381-8 and classified by EN 13501-2. This test do not cover other aspects that relevant to reactive coatings, such as fingerprinting for ID issues, moisture resistance for external application, stability in shelf life. EOTA (European Organization for Technical Approvals) developed years ago an ETAG (European Technical Assessment Guide) with the scope of complementing EN test (ETAG 018/2). [1, 2, 3]

Therefore, reactive coatings tested for resistance to fire according to EN13381-8, classified according to EN 13501-2 and technically assessed as per ETAG/018 having obtained the related ETA (European technical Approval), can have the CE marking for the product.

The Construction Products Regulation in Europe indicates that only products with CE marking coming from harmonized EN standard are obligatory in Member States, we are not there yet so CE marking for reactive coatings is today a quality assurance for users rather than an obligation.

Reactive coatings manufacturers are working to change that, the industry sector has developed in CEN TC139 WG13 a new standard for reactive coatings covering the points as per ETAG 018/2. The new standard EN 16623/2015 is not harmonized and therefore not yet compulsory. However, the EC (European Commission) has ready a draft mandate to CEN for a revision of this EN to be upgraded to hEN (harmonized).

CE marking for reactive coatings will be compulsory all over the EU in the future.

EN 16623 basically describes what the reactive coating manufacturer have to detail about the coating besides fire test results already reported as per EN13381-8.

The most critical points are:

- Defined Ingredients - details what to do in case the Paint manufacturer would like to replace an ingredient, different levels of influence in the formulation mandate different procedures (see table 2),
- Coatings Formulations - Under the concept that “ what was tested is what have to be applied”, some paint parameters called <u>fingerprints</u>, for example IR pattern and TGA, have to be shown by the manufacturer to the users,
- External Exposure - The coating could be classified as internal only, semi external or external application (see table 3). The EN norm covers in detail this point, <u>water contact resistance</u> is crucial to qualify for external application.

Next steps in the EU norms developments.

- Application - Coating application is an area of concern, a bad application can impair the efficiency of the best coatings, an European Guide for Installation of Passive Fire protection products, which include reactive coatings, issued by

CEPE (European Confederation of Paint Manufacturers) and EAPFP (European Association for Passive Fire protection), will be included in the next revisions of the CPR.

- Coating Viscosity over time - One particular point is coating shelf life and Viscosity, reactive coatings tend to thicken with time, if the paint is too thick the applicators may have an increasingly hard time to achieve the requested DFT, to the point of not being able to apply the necessary amount of material and leave the structure poorly protected. In fact it is a major concern that the dilution with solvent to enable the application by airless or brush, is very often higher than specified, and therefore the final DFT is not the same as tested and reported in the certificates

Table 2

Component/raw material	**Situation/circumstance**	**Fire test level**	**Effects performance**
Acid source (e.g. APP)	Change of grade or supplier.	5	Yes
Binder	Change of the supplier of the resin binder used in type testing.	5	Yes
Plasticiser	Change of resin, molecular weight or grade.	5	Yes
	Alternative supplier of same material as used in type testing, same assay and particle size distribution.	3	No
Blowing agent (e.g. melamine)	Change of resin, or grade.	5	Yes
	Alternative supplier of same material as used in type testing, same assay and particle size distribution.	2	No
Reinforcement (e.g. fibre)	Change of material type or fibre length, particle size distribution.	5	Yes
	Alternative supplier of same material as used in type testing, same assay and particle size distribution.	2	No
Carbon source	Change of grade e.g. purity, particle size distribution.	5	Yes
	Alternative supplier of same material as used in type testing, same assay and particle size distribution.	2	No

Table 3

Type	Exposure Description
X	intended for all conditions (internal, semi-exposed and exposed)
W/Y	Temporary full external for a maximum of 6 months then semi external
Y	intended for internal and semi-exposed conditions. Semi exposed includes temperatures below zero, but no exposure to rain and limited exposure to UV. (UV is not assessed)
W/Z1	Temporary full external for a maximum of 6 months then internal with high humidity
W/Z2	Temporary full external for a maximum of 6 months then internal with controlled environment
Z1	intended for internal conditions (excluding temperatures below zero) with high humidity
Z2	intended for internal conditions (excluding temperatures below zero) with humidity classes other than Z1 These conditions apply for internal humidity class 5 in accordance with EN ISO 13788

4- AMMONIUM POLYPHOSPHATE AS KEY INGREDIENT.

Ammonium polyphosphates APP are classified as level 5, which is the highest level of influence in the Fire protection of a Coating for an Ingredient, APP also have an heavy influence on other important performances of the products. Budenheim is making APP since a few decades, we have developed specific grades for specific applications as well we apply very sophisticated manufacturing technologies to guarantee constantly materials quality.

Currently we have an active R&D program, also in partnership with the Industry players, with the following targets:

- SHELF LIFE - Develop APP's which improve coatings shelf life
- EXTERNAL EXPOSURE – Develop APP's for paint application in wet environment
- FINGERPRINTING – Measure APP quality and its influence in Coatings performance

<u>REACTIVE COATINGS SHELF LIFE</u>

Shelf life of reactive coatings may be influenced by external factors such as warehousing conditions, time, packaging, but the key to keep a stable Viscosity lies with the Ingredients. It is known that low quality Ammonium Polyphosphate may strongly contribute to viscosity rise, this phenomenon could create huge problems in water based systems application.

Budenheim has developed a modified APP that does nearly eliminate viscosities rise over time, the tables below show the evolution of the viscosity over time for a water based “standard” formulation using three different APP’s. The new APP FR CROS 584 show the optimum performance regarding stability and represents a huge improvement in such important aspect that is the shelf life of the paint and the proper dilution at the application site, allowing ease of use and real safe protection of the structure.(Figures 4 and 5).

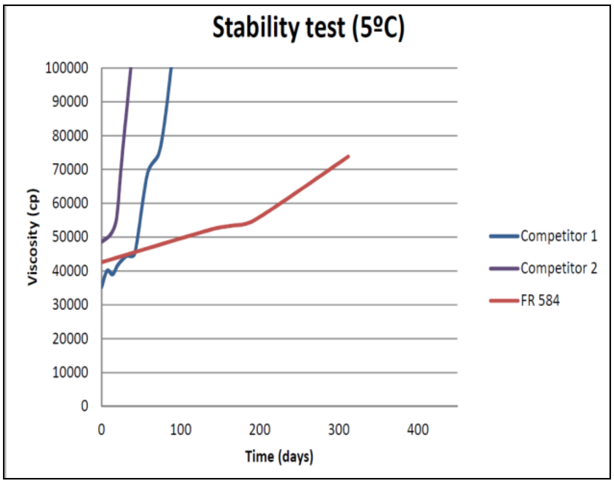

Figure 4

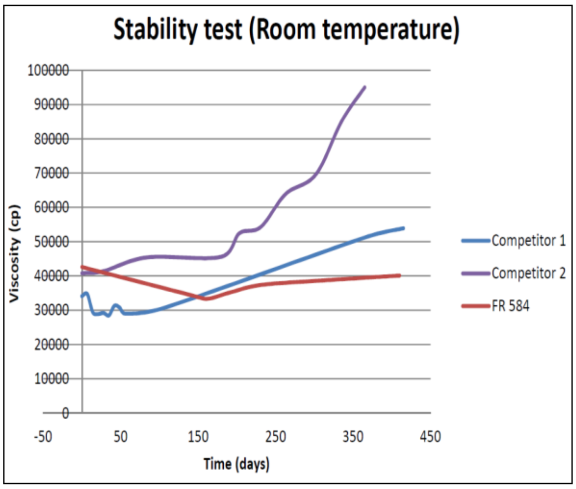

Figure 5

REACTIVE COATINGS EXTERNAL EXPOSURE

During the installation process, the applicator has to follow the indications of the classification of the paint: X for external, Y for semi external and Z for internal only. Such classification refers not only to the building end use, but as well at the construction period. E.g. a paint classified for internal use only, shall not be applied when the building is not yet roofed because such paint do not resist water.

Therefore, a proper formulation has to be developed for each of the conditions set forth here above. The most demanding application is the one for external use: clearly here the ingredients have to be very highly water resistant and among them, ammonium polyphosphate is one of the most critical: low quality APP may be hydrolyzed by dry coating exposure to wet conditions to the point or rendering the coating non efficient

Ammonium polyphosphate is a condensation polymer where water is removed to condensate ortho monomers, water can hydrolyze back the polymer to ortho monomers. These phenomena depend on the polymerization index and other parameters that have to be maintained during APP manufacturing.

Resistance to hydrolysis of Ammonium Polyphosphates is only achievable by two means: a) the high quality of the polymer, and the most important b) microencapsulation of APP (Figure 6)

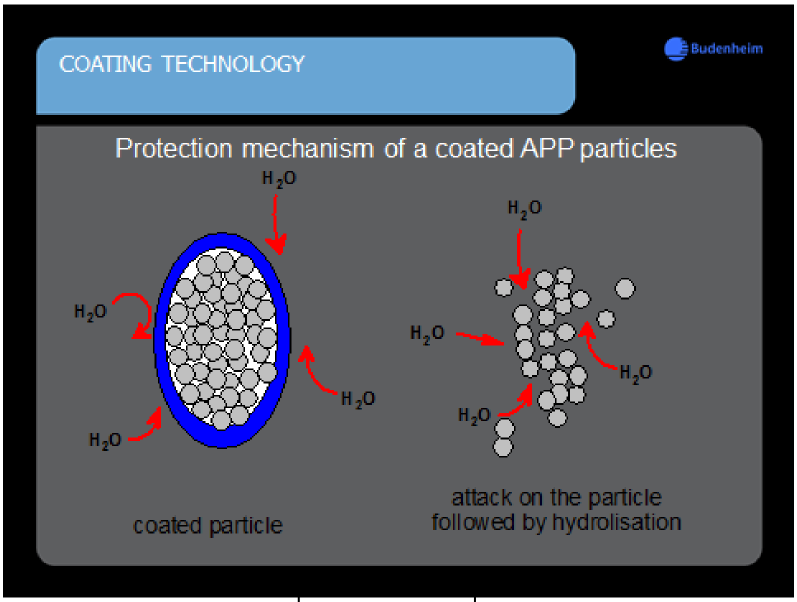

Figure 6

To prove that particular point, we have tested a coating containing different types of APP:

- FR Cros 484 – Standard APP II, water solubility 0,4 g/100ml
- FR Cros 487 – Microencapsulated shell coating, water solubility 0,1 gr/100 ml
- FR Cros 489 – Microencapsulated with a chemical reaction, water solubility 0,01 g/100 ml.

The metal coupons coated at a DFT of 1000 microns were stabilized for a certain time and temperature in an oven and then partially immersed in the water 24h at room temperature as an extreme moisture resistance test.

The pictures below (Figure 7 –FR CROS 489-, Figures 8 –FR CROS 487- and Figure 9 –FR CROS 484-) show clearly that the better the lower the water solubility the better the resistance to blistering. This test could correlated with type X,Y and Z respectively.

Figure 7

Figure 8

Figure 9

Coatings Fingerprinting

ETAG 018/2 describes the fingerprinting as the data obtained by the Dry Film of the paint after milling to a very fine powder and tested with defined methods determining TG, IR spectrum of the collected fumes after submitting the sample to heat and IR spectrum of the product.

EN 16623 is more open and leave up to the manufacturer the detailed method for determining de fingerprints, although suggest to apply thermal gravimetric and IR methods.

Being APP one of the key ingredients, the above mentioned parameters have been studied in the same formulation but changing the APP types. The results show that:

TGA: have to be very precise as to identify differences (See Figure 10)

IR of the collected fumes: no difference (this test intended for VOC determination)

IR of the product: no difference. See Figure 11.

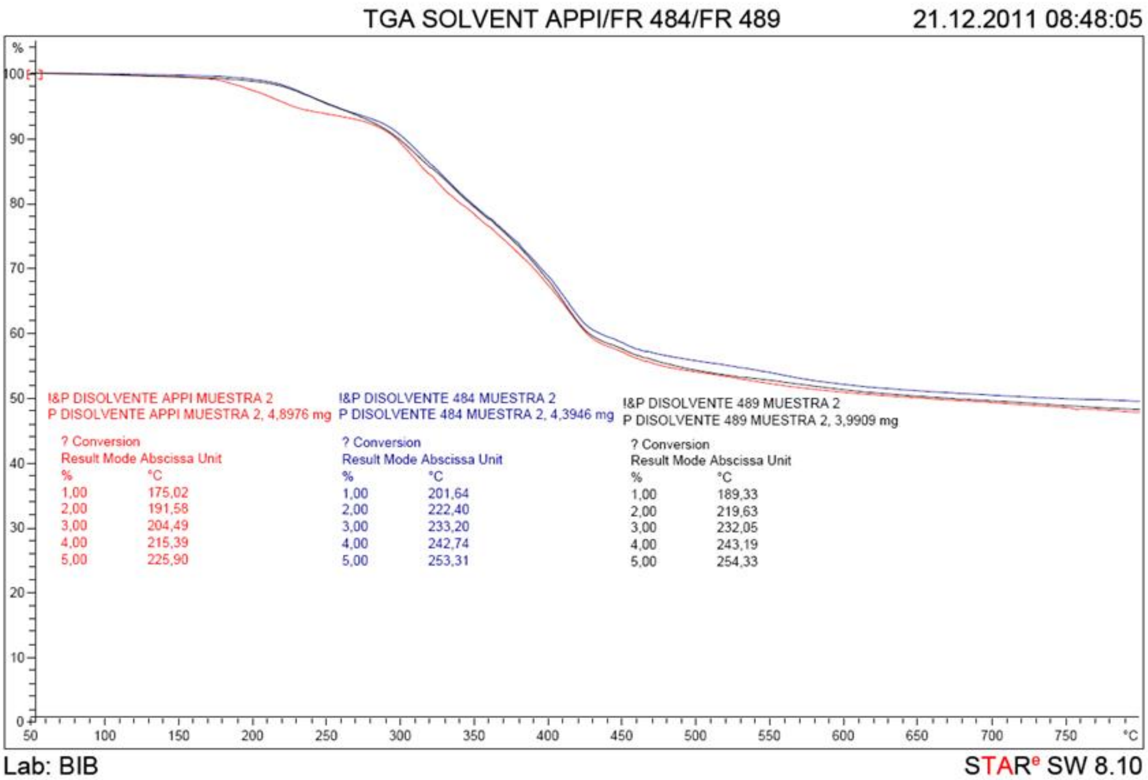

Figure 10

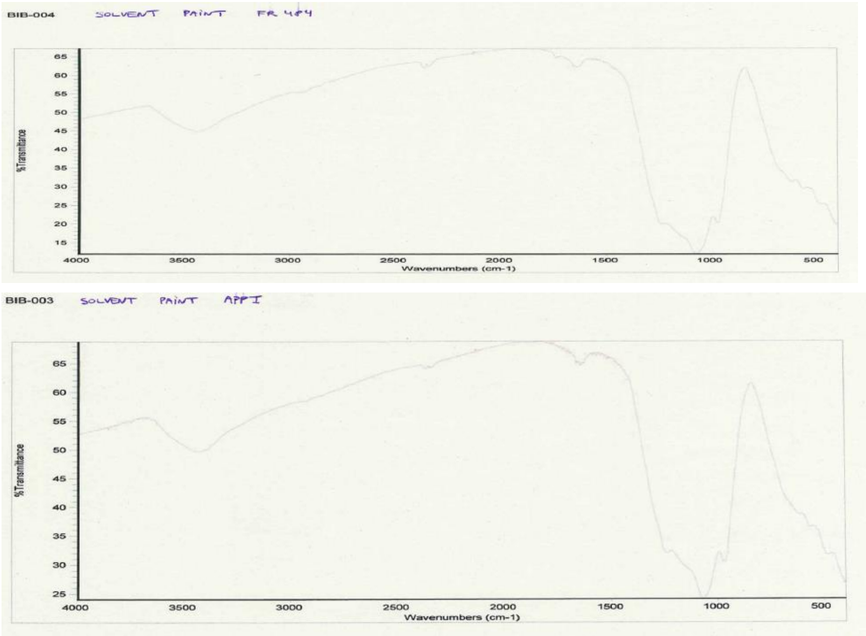

Figure 11

Under such poor differentiation, we have developed other methods that can help in such fingerprinting process.

We tested water solubility of the Dry Films, and clear differences could be correlated only to the different APPs as can be seen in table below:

Paint	**APP**	**Solubility (g/100 ml water)**	**P_2O_5 ****	**Solubility 24 H ***
Water	APP I	Paint does not possible to be manufacture		
Water	484	1,8	0,134	51,76
Water	487	1,679	0,278	48,09 / 48,25
Water	489	1,64	0,106	46,85
Solvent	APP I	2,27	0,847	41,39
Solvent	484	1,003	0,08	51,61
Solvent	487	0,782	0,214	50,17 / 47,88
Solvent	489	0,868	0,064	47,35

We tested for X-ray diffraction pattern and could clearly identify in the Dry Film the crystalline nature of the APP (APPI, APPII) without interferences from the other ingredients. No difference found between coated and non-coated grade. See Figure 12 below.

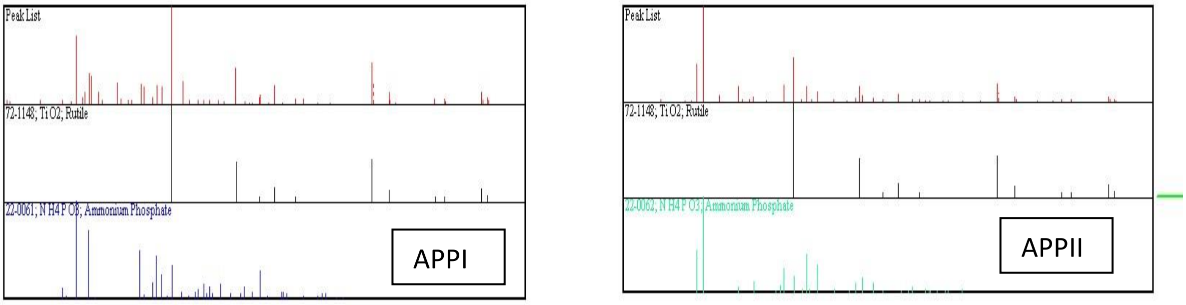

Figure 12

5- Conclusions

As a conclusion, we may say that in order to guarantee high level of safety, adequate normative for Passive Fire Protection have to be combined with effective means of control on site. Paint stability for correct installations, fingerprinting for on-site inspection and external exposure resistance, are key properties for achieving high levels of safety using reactive coating, the type and quality of Ammonium Polyphosphates play a key role on these parameters.

Budenheim has a strategic commitment to Fire Safety, leading innovation in this field with new products developmnet, cooperating with regulatory bodies to upgrade testing methods and regulations, having joint R&D projects with coatings manufacturers.

6-References

[1] EN 16623 CEN TC 139   *Paints and varnishes. Reactive coatings for fire protection of metallic substrates. Definitions, requirements, characteristics and marking*, 2015.

[2] ETAG 018/2 EOTA *Fire protective products, Part 2: Reactive Coatings for Fire Protection of Steel Elements.* Date of endorsement 06/12/2011.

[3] EN 13381/8 CEN TC 127 *Test methods for determining the contribution to the fire resistance of structural members. Applied reactive protection to steel members*, 2010