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Article

Carelessnes in Morphology Design Can Affect Organic Coatings Performance

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Abstract: In many instances paints interlayers delamination is attributed either to environmental or to application reasons. The composition as well as the structure, including morphology are always given for granted. The resin to pigment ratio, the surfactants, the quality of pigments and fillers (dimensions, shape, wettability, reactivity, homogeneity of distribution…) are not clearly required, defined and consequently checked. A fundamental article appeared in 1949 defining PVC and CPVC. In the following, it was quoted several times but not many improvements in the subject were shown: the subject was considered as obvious and unquestionable. We have tested some cases of coating delamination from big steel structures where other causes were either absent or not dominating if paint features were not taken into account. Many features of paint composition and structure were analyzed with both SEM and EDAX and a comparison with a carefully formulated paint was carried out.

Keywords: delamination, CPVC, pigments, fillers, extenders, topography

1. Introduction

If a paint is used to reproduce reality as an object of art, or to give a decent aspect to a building or actually to protect a structure against degrade, always both durability and reliability are of concern.

In particular, protecting coatings for structural steel are formulated and applied in billions of square meters to the aim of avoiding or at least delaying both aesthetic and dangerous degradation, providing a predictable long service life to bridges, plants, skyscrapers, cars.

This aim in many countries is not checked and certified by authoritative bodies as it happens to those materials which are classified as "building materials" (classification depends on the country) but their quality is instead left in the hands of "Standards" under the agreement and mutual control of the parties involved in a project. These Standards cover some specific properties and features and are connected with "requirements" also agreed by the parties according to the expected durability in a classified aggressiveness of an environment.

The standards are mainly if not exclusively concerned with performances and related to such parameters as both number and thickness of layers, hardness, adhesion (expressed as the strength needed to remove the paint from the substrate), gloss, scrub resistance, corrosion resistance, porosity etc.

Such parameters depend obviously on the care and wisdom in both formulation and proportions of components, which is not an easy task, from both scientific as well as technical and last but not least, economical points of view.

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Paint is a complex composite material, containing:

- pigments to impart both color and opacity,
- binder (resin) - a polymer, (the resin), with the task to hold the pigment in place
- extender(s) or “inert(s)” - various pigment particles added to strengthen the film and save more expensive binder,
- solvent (sometimes called thinner) - either an organic solvent or water is used to connect the ingredients and/or reduce the viscosity of the paint for better application,
- additives - used to modify the properties of the liquid paint or dry film, which may include:
    - dispersants - to separate and stabilize pigment particles,
    - thixotropic agents – used to modify viscosity under fluodynamic conditions (practically stirring),
    - driers - to accelerate drying time,
    - anti-settling agents - to prevent pigment settling,
    - bactericides - to preserve water based paints in the can,
    - fungicides and algaecides - to protect exterior paint films against discoloration from molds, algae and lichen.

A further differentiation in formulation is according to paints proposed use: primer, undercoat, special finishes (matt, gloss, heat resistance, anti-corrosion, abrasion resistance). The pigment powder is broken down into individual particles which are coated by and dispersed in the resin - known as 'wetting out'. Solvent is then added to give the required consistency.

Primers may be pigmented with metallic elements anodic to steel. When a break in the coating exposes the steel substrate, the anodic metal corrodes sacrificially in preference to the steel. Zinc-rich primers are the most commonly used.

Primers are also used containing inhibitive pigments to interfere with the corrosion process. Zinc phosphate, for example, is a mildly inhibitive pigment and is widely used in modern primer formulation, in combination with a strong adhesion and a carefully clean surface.

The undercoats (or intermediate coats) are applied to ‘build’ the total film thickness of the system. Generally, the thicker the coating the longer the life. This may involve the application of several coats. Undercoats are specially designed to enhance the overall protection and, when highly pigmented, decrease permeability to oxygen and water. The incorporation of laminar pigments, such as micaceous iron oxide, reduces or delays moisture penetration in humid atmospheres and improves tensile strength. Undercoats must remain compatible with finishing coats when there are unavoidable delays in applying them.

The instable and complex equilibrium among the very many chemically reactive and specifically useful components is at the basis of the quality of the final product, the paint, as well as a watch is as precise and precious as it is the quality of both widely used components and their multi-reciprocal compatibility.

A first qualitative approach to the virtuous symbiosis of liquid- solid components has been studied in the forties of last century in Germany and given an understandable and workable shape by Asbeck and Van Loo [1]; after their deep and careful approach to the problem, their conclusions are still valid and widely used:

% PVC = volume of mineral x 100 / (volume of mineral + volume of resin solids)

Many basic properties of paints are affected both positively and negatively by the PVC ratio. Asbeck and Van Loo studied the relationships and coined the term CPVC (Critical Pigment Volume Concentration) The volume that the mineral, sum of pigments and extenders, occupies in the matrix and its ratio to the volume of binder plays an important part in the properties of the paint. Pigment volume concentration (PVC) is an important parameter when formulating paints and coatings. The oil absorption of the minerals must also be accounted for. The amount of resin left, after the oil absorption has been satisfied, is the "free binder**". The amount of free binder affects factors such as gloss, adhesion, corrosion resistance and durability**.

At values lower than CPVC there is an excess of binder. This results in high gloss, good scrub resistance, good corrosion resistance, good blister resistance and good adhesion. At values over CPVC, there is insufficient binder to **completely coat all the mineral particles.** This results in low gloss, poor scrub resistance, poor corrosion resistance, poor blister resistance and poor adhesion. It is recommended that the coating be formulated either below or above CPVC but not at CPVC, since properties change rapidly at CPVC, and very minor differences from batch to batch can result in major differences in properties [1].

A very interesting paper on the subject was written by Rodriguez and alii [2]. It will be important to report here their conclusions, based on accurate Electrochemical Impedance spectroscopy measurements: "Anticorrosion coating performance is affected greatly by PVC/CPVC ratio. It has been concluded that in high crosslinked systems it is recommended the use of **low pigment content** in order to obtain better **anticorrosion** properties although **the final coating can be more expensive**."

The importance of CPVC is outstanding, but unfortunately does not cover the full evidence of the problem. A very interesting presentation is available in the web from Vanderbilt Minerals, LLC [3] and even more thoroughly approaching the topic is a Handbook & Formulary "INDUSTRIAL MINERALS AND THEIR USES" [4].

In these papers, it is clearly pointed out that the effects of addition of minerals to paints and coatings depend on: mineralogy (chemistry, crystal structure, Mohs hardness, etc.) oil absorption, brightness, pH both value and variation, chemical inertness, refractive index, purity, soluble salts, particle size and particle size distribution; particle shape and aspect.

When such parameters are not taken into appropriate consideration, a very probable effect is on durability, since the binding power of the resin might mask, in the short term, the lack of interface equilibrium and the defects are suitable to affect mainly adhesion in the medium - long period.

One should also consider carefully that, as requested by all widely used standards, paint systems are tested and "certified suitable" for a class of both durability and environment on the basis of a number of samples produced by the official laboratory, which will assert that the results "refer exclusively to the tested samples" with a given set of physical-chemical-mechanical-morphological features of solids, a given PVC, leaving alone the quality of the binder as well of other additives.

In the absence of a check of such parameters, any possible failure will be attributed to either environmental or application diversities, applying a "bona fide" concept to the possibility that a mistake in the pigment percentage, or a replacement of, say, good, wettable, plate, flaky talc with

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some cheap carbonate, a fine grain size with coarse, inhomogeneous rocks will affect in opposite directions both value and durability of the paint.

2. Materials and Methods

In this paper, we'd like to point out, on the basis of practical, on-site examples that the study of paint morphology on a microscale might be crucial for understanding the actual mechanisms of a failure like an early interlayer delamination. Often this phenomenon is attributed to either excessive time elapsed before overcoating, or to amine outcrop, or even to UV degradation and chalking or bad surface preparation. Since all and each one of such events are likely to actually have been happened, it appears not necessary to investigate on other possible mechanisms. In one of the cases examined, (in the following named 1U) the extension of delamination was so high, and the possible reasons of it were so many, including UV, time of overcoating, possible polyamine outcropping, that no investigation was supposed necessary on possible defects in the formulation of the system

It was possible for various reasons to collect in the IBDiM Anticorrosion Laboratory in Warsaw a number of paint samples recovered after detachment from various locations of the structure. A comparison was possible of such samples with other ones obtained using paints of the same label either present in the Laboratory as reference or bought directly on the shop.

The morphology of the mineral components: SEM micrographs of both the cross sections of the samples and of the surfaces detached from the overcoat, as well as of the surface of the samples prepared in the laboratory using the "standard" paints were obtained using a JOEL 6010 LV with EDX. Scanning Electron Microscope. The photos were analyzed with a surface analyzing program and the size and amount of filler/extender/pigment particles were counted and compared.

The analyzed samples showed in this article were:

a) A first series of samples taken from a partly immersed - partly exposed to marine atmosphere where diffuse delamination was observed. An example is shown in fig.1a and b. It was a polyamine cured high built epoxy mastic intermediate coat (Norsok certificate for HD IM) which delaminated from the epoxy mastic primer (samples called 1U in the following).

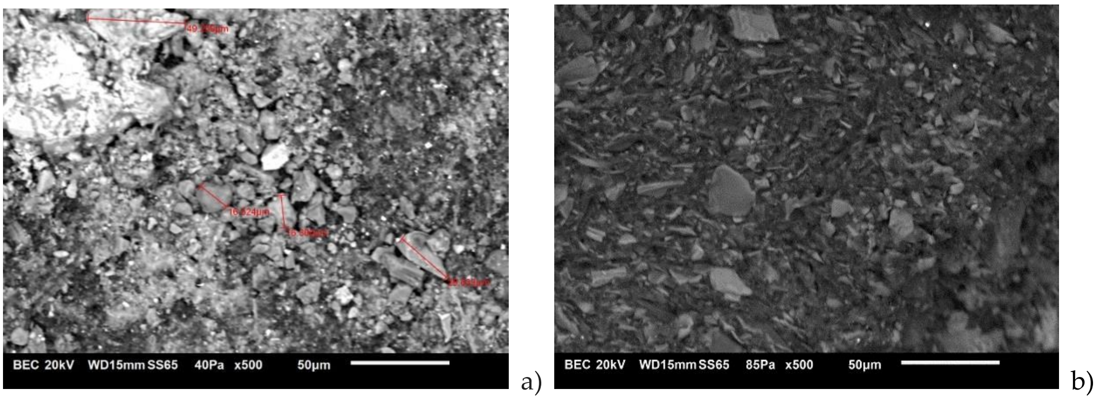

Fig.1: SEM micrograph of the delaminated surface (fig.1a) and cross section (fig.1b) of sample 1U

b) A second series of samples of the same brand with the same label but directly bought on the market (samples called 1 in the following). An example is shown in fig.2a and b.

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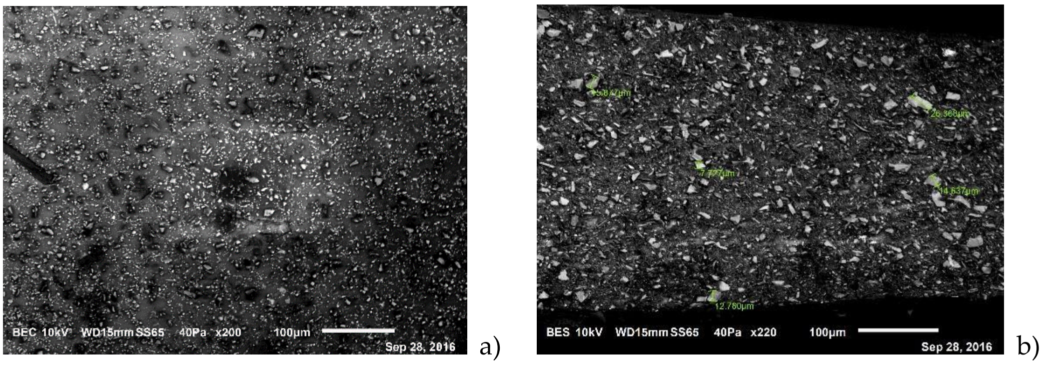

Fig.2: SEM micrograph of the surface (fig.2a) and of the cross section (fig.2b) of sample 1

c) One series of samples (epoxy intermediate and siloxane topcoat as related to ISO12944 class HD C5) taken from a bridge where no failures were observed (samples called **2** in the following). An example is shown in fig.3a and b.

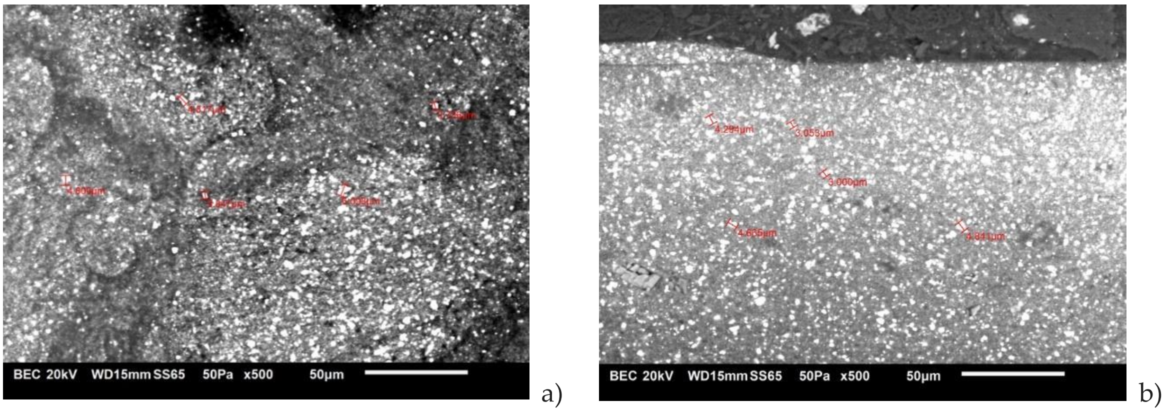

Fig.3: SEM micrograph of midcoat surface (fig.3a) and cross section (fig.3b) of sample **2**

d) A second series of the same kind of paint taken from a structure where diffuse delamination between intermediate and topcoat were observed (samples called **2U** in the following). An example of delamination is shown in Fig.4a and b.

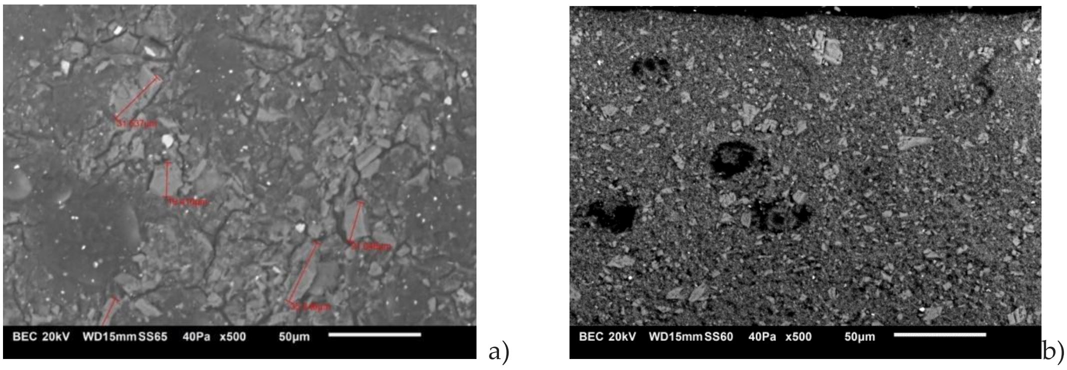

Fig.4: SEM micrograph of the delaminated polysiloxane surface (fig.4a)
and of cross section (fig.4b) of sample **2U**

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3. Results and discussion

We analyzed four cases of application of systems considered as suitable for long service life (high durability, according to standards) in harsh environment (C5, IM). The two systems were formulated and composed according to different design, but in principle expected to produce the same performances.

Actually, in case "C" no failure was found after 12 years. Samples produced with the same batch of paint in the laboratory gave the results which are shown in both SEM micrograph (fig.3a and fig.3b) and in topographical analysis. The good performances are clearly due to a correct use of the right amount of well distributed, low dimension, low concentration both pigments and extenders. They are also well wetted by the resin, with no void and no crevice between pigment and binder.

As for case **1U**, a systematic morphological study of a reasonable number of samples collected in different locations where they delaminated (15 samples) provided evidence that a very low percentage of the resin in the interphase surface is left available for interlayer bonds by the coarse, crowded, partly wetted both extenders and pigments (detailed photo of pigment only partly wetted by binder is shown as Fig.5.

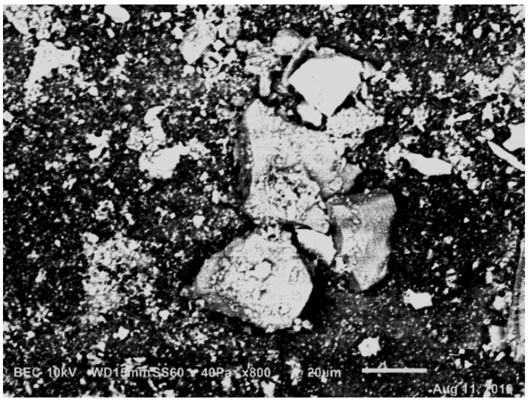
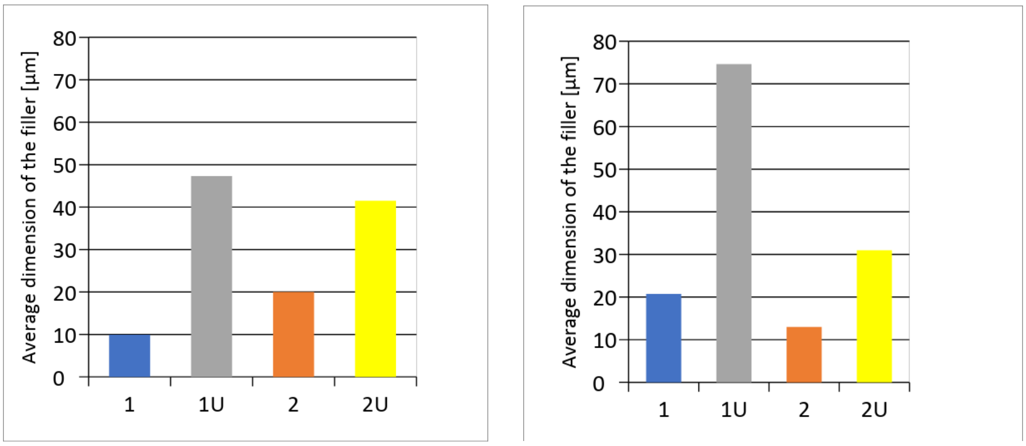


Fig.5: Fillers only partly wetted by the binder of sample 1U

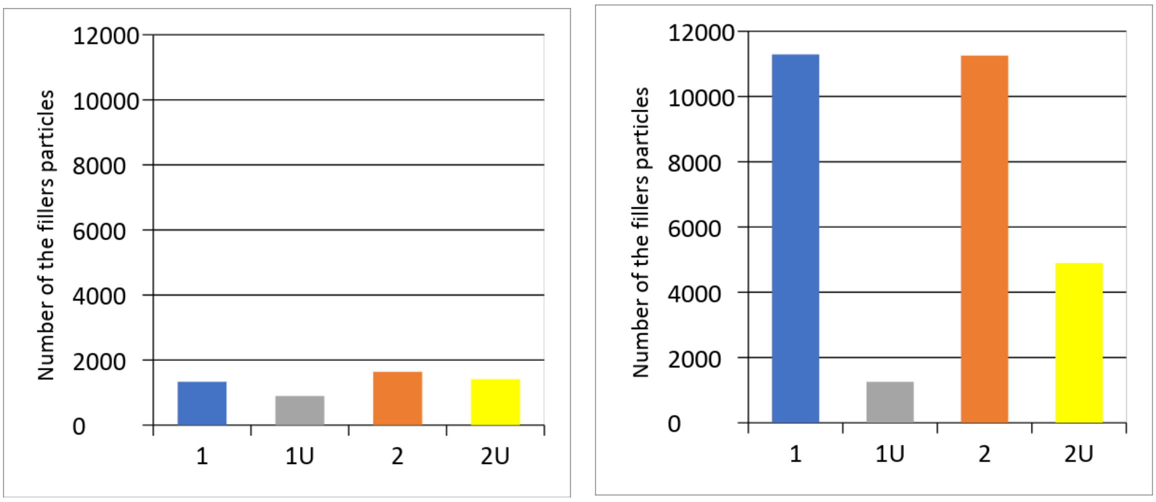
The failures claimed in case **2U** are coherent with an excess of pigment size and concentration, a coarse distribution of their dimensions, an excess crowding at the interface. Pigments (extenders) are in many instances clearly not wetted by binder. A typical example of such behavior is displayed in fig.4a and fig.4b.

The comparison of the statistical topographical analysis gives an even more quantitative evaluation of the phenomenon. Actually, the SEM analysis with a suitable program of acknowledgement of different tonalities of gray allowed to evaluate the average dimensions of the particles (fig.6), the number counted on both surface and cross section (fig.7), the amount of area occupied by the particles, (fig.8) the max. – min. diameter values (fig.9). A comparison of the values relevant to the defective and to the standard systems shows the tremendous existing differences. It looks like that the surface allowed to the binder as well as the lack of smoothness of the interface itself, leaving alone the crevices left by the insufficient wetting (see e.g. fig.5) hindered the establishment of a durable interlayer bond. As an example, comparing the topographical results as related to samples 1 and 1U, it is evident that in the latter the dimensions of filler particles were such as to occupy an excessive percentage of the available area, even if their number was lower than in sample 1. Moreover, comparing for the same purpose samples 2 and 2U, it is evident that the dimensions of particles is also the responsible of early delamination, while in the case of samples 1U, even worse effects were caused by an excessive concentration of coarse particle at the interface.



a) b)

Fig.6: Average dimension of the fillers measured on surface a), and cross section b) of tested samples



a) b)

Fig.7: Number of the fillers particles counted on surface a), and cross section b) of tested samples

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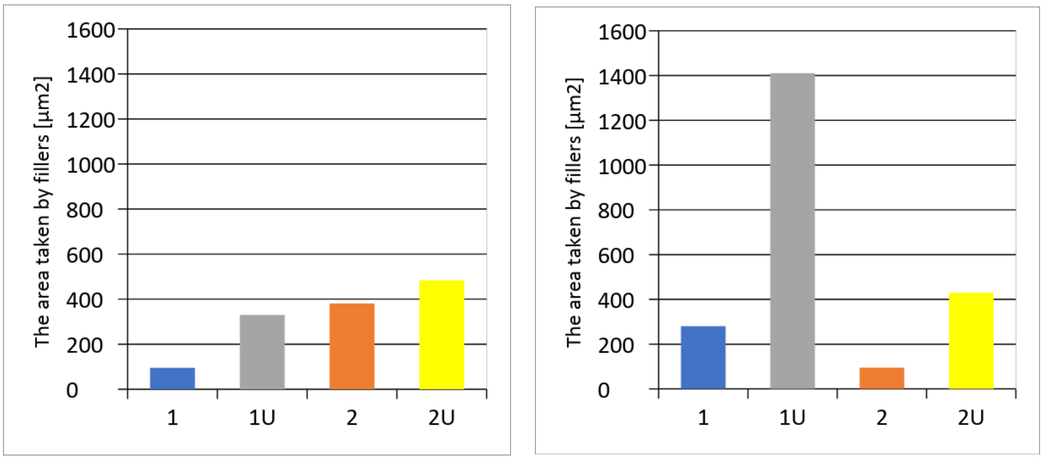
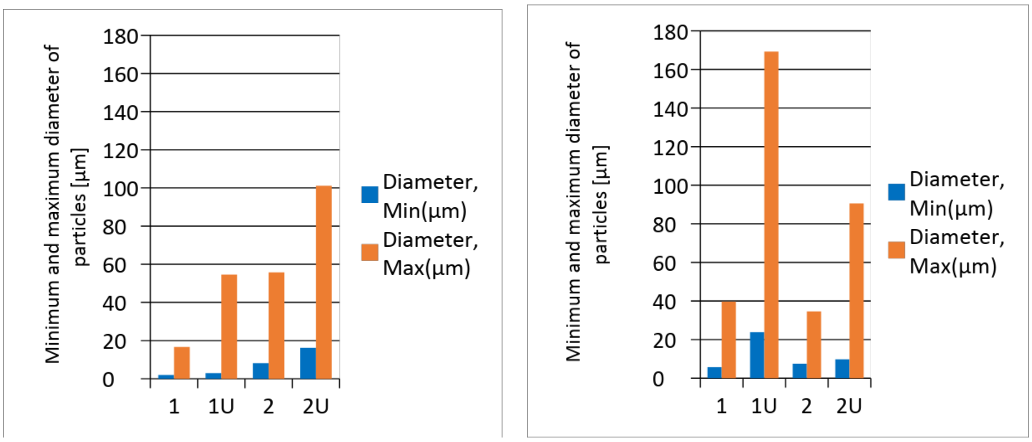


a) b)

Fig.8: The area taken by fillers measured on surface a), and cross section b) of tested samples



a) b)

Fig.9: Minimum and maximum diameter of elements measured on surface a) ,and cross section b) of the tested samples

4. Conclusion

Inert pigments, the ones which are neither anodic nor inhibitive, are not so a “sine cura”, as it had been supposed until now. Their particle size, the presence of aggregates and agglomerates, their wettability by the binder and, consequently, their tendency to accumulate water at the pigment/binder interface if the film is subjected to water are important to the durability and to the efficiency of a protecting coating. A technical approach to the choice of pigments, not only relevant to their economical role in reducing the amount of the “rich” resin, and not only inherent to the CPVC distance, but also to avoid that their accumulation might reduce the space allowed to the binder necessary to assure a suitable and long-lasting interlayer bond. The good paints performances are clearly due to a correct use of the right amount of well distributed, low dimension, low concentration both pigments and extenders, which have to be well wetted by the resin, with no void and no crevice between pigment and binder.

The authors shyly suggest that some paragraphs in the existing Standards should deal with stricter specifications concerning both PVC and the kind and size of pigments to be used.

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