Determination of micro-indentation hardness of organic coatings

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Abstract

Many industrial products have to be coated by organic materials not only for aesthetical reasons, but specially to prevent the integrity of the metallic substrate from corrosion attacks during their service life; then, the corrosion resistance of metallic component is often assigned to the physical properties of the coating material.
A lot of specific tests are available in the field of surface treatment characterization, in order to assess mechanical, physical and durability properties of paints and varnishes.
Among them, indentation hardness allows to investigate on the local properties of a painted layer, not only on the external surface but also into the coating thickness, making it possible to verify hardness at every depth of the layer; non-uniformity in hardness values can be referred to the painting process (curing conditions, coating material, etc.).
Hardness measurement technique on the transversal section required particular attention in the specimen preparation; hardness tests were performed by using a Knoop indenter, according to the standard ISO 6441-1.
In the present paper are reported the results of several hardness tests performed on the surface and on the transversal section of various aluminium painted samples, some of them partially polymerized to different degrees. The same results have been compared with the results of commonly used tests for coating characterization, as: Taber abrasion test, hardness pencils test, Buchholz indentation test and also impact test.

Introduction

Organic coating characterization is often performed by means of technological tests (bending, cupping, scratching, abrasion, impact test) because the results can provide a direct correlation to the coating behavior during the next work process or utilization; in these cases the results are given in the qualitative form “pass-fail test”.
Some experimental methods based on local characterization, as “hardness measurement” can be more suitable to achieve a better understanding of the coating properties in the whole layer, with the aim to find any improvements in the coating performance.
Micro-indentation technique, generally used to investigate about the film hardness on the surface (as foreseen by current practice standards), can be applied also to investigate through a cross-section of the layer and study fine scale changes in hardness.
In this paper the results obtained from some typical tests for organic coating will be compared with the ones obtained from micro-hardness investigation trough the cross section of the same layer.

Experimental

Sample preparation
The film was applied on flat cold-rolled aluminum alloy EN AW-5005, dimensions 300 x 100 mm and thickness 1,0 mm. Prior to application of the coating, the aluminum surfaces were prepared with a chromium-based chemical treatment.

A commercial polyester powder coating (TGIC free and glossy type – RAL 6012) was then applied by electrostatic spray on the test panels mounted on proper holders, taking care of producing uniform deposition of the powder.
Since the properties of a powder coating can vary considerably with its thickness, the test panels were produced with two different thickness (LT – low thickness, HT – high thickness). After spraying, the test panels were cured in an oven for the time and the temperature recommended for the specific powders used (180°C for 20 minutes). Some test panels were overbaked (210°C for 20 minutes) or underbaked (160°C for 10 minutes) to magnify the time/temperature effect on the physical properties of the film. In all cases the temperature was monitored on the metal substrate by means of thermocouples connected to a data logger display.
The film thickness and gloss of the test panels were measured, obtaining the mean values reported in table 1. It was found that the film thickness could vary within ± 5% of the calculated average value.

Sample	**Coating thickness ISO 2360 (μm)**	**Gloss (60°) ISO 2813**
160 LT	95	88
160 HT	156	87
180 LT	97	90
180 HT	164	89
210 LT	85	88
210 HT	178	86

Table 1. Average values of film thickness and gloss

Before testing all the panels were conditioned for 24 h at 23±2°C and 50±5% relative humidity; the following tests were conducted in the same environment.

Instrumental techniques

Resistance to abrasion (Taber abrasion test)

- The organic layer resistance is usually established by TABER abrasion tests (ISO 7784-2 and ASTM D 4060) using specific abrasive wheels and the "abrasion resistance" is calculated as loss in weight at a specified number of cycles. Resilient calibrase wheels No. CS-10 were used, applying a 1000 g load for a total of 2000 cycles in four steps (the wheels were resurfaced every 500 cycles with S-11 abrasive disk). The test specimen (100x100 mm) was weighed before the abrasion and after the completion of every 500 cycles, calculating the weight loss (mg). The results (average values of two tests) are summarized in the bar graph of figure 1:

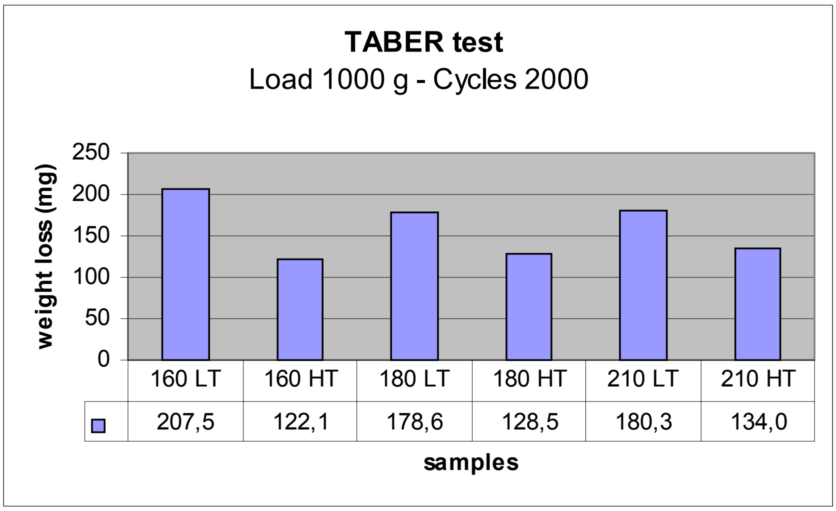

Figure 1. Taber test results

Hardness pencils test (ISO 15184)

- The purpose of the pencil test is to determine the hardness of an organic coating referring to the hardness scale of the pencil leads. This practice, usually performed manually, is useful in production control testing but the results obtained may vary between different operators. To obtain more accurate measurements the tests were performed using a mechanical device that allows to reproduce the fundamental test conditions (load of 750±10 g and pencil inclined at an angle of 45±1°). The results are given in table 2, in terms of “the hardest pencil which does not mark the coating”:

Samples	Pencil hardness			
	HB	F	H	2H
160 LT	P	F	F	F
160 HT	P	F	F	F
180 LT	P	P	F	F
180 HT	P	P	F	F
210 LT	P	F	F	F
210 HT	P	F	F	F

P = pass F = fail

Table 2. Pencil hardness results

Buchholz indentation test (ISO 2815)

- This test method allows to determine the surface resistance to indentation of an organic coating, using a specified instrument. This practice is particularly sensitive to the positioning and removal of the apparatus, as well as to the recovery time before measuring the indentation length. The test result is expressed as a function of the reciprocal of the indentation length and this value increases as the resistance to indentation increases
  In table 3 are summarized the results as the mean value of five tests carried out on the same test panel.

Sample	Indentation length (mm)						Indentation Resistance
	1	2	3	4	5	average	
160 LT	1,2	1,1	1,2	1,2	1,1	1,16	**87**
160 HT	1,1	1,2	1,15	1,2	1,15	1,16	**87**
180 LT	1,0	1,15	1,15	1,15	1,15	1,12	**91**
180 HT	1,1	1,1	1,1	1,15	1,15	1,12	**91**
210 LT	1,0	1,05	1,05	1,0	1,0	1,02	**100**
210 HT	1,1	1,05	1,1	1,1	1,1	1,09	**91**

Table 3. Buchholz indentation test results

Impact test (falling-weight test ISO 6272)

- Impact test was carried out to determine the minimum drop height and mass causing cracks in the coating. All the panels were tested with the coated face down, clamped on the die, without using stops to limit the indentation depth of the falling weight. Successively greater heights of weight-release were adopted, with a falling-weight of 1000 g or 2000 g, until cracks were detected. The results, expressed as the maximum energy (Joule) that the coating is able to withstand without cracking, are summarized in table 4.

Samples	Energy max (Joule)
160 LT	0,3
160 HT	0,3
180 LT	20
180 HT	3
210 LT	20
210 HT	10

Table 4. Maximum energy withstood by the test panels

Knoop hardness test (surface)

- ISO 6441-1 and ASTM D-1474 deal with standard test methods for indentation hardness of organic coating when applied to a plane rigid surface. The apparatus was pre-set to apply a Knoop indentation with a 25 g load for 18 seconds normally to the surface to be measured. The length of the long diagonal of the impression was determined by means of a semiautomatic measuring system. The procedure was repeated in five widely spaced locations for each test panel and the results were expressed as the mean value (see table 5).

Samples	HK 0,025 Mean value
160 LT	15,4
160 HT	15,6
180 LT	15,0
180 HT	15,0
210 LT	14,6
210 HT	15,0

Table 5. Surface Knoop hardness results

Knoop hardness test (cross-section)

- This procedure is not standardized for organic coatings by ISO 6441-1 nevertheless micro-hardness measurements were carried out taking into account ISO 4516 standard (related to metallic coatings). To ensure the planarity of the cross-section test surface, specimen were cold mounted in acrylic resin and properly polished.
  In these tests a load of 10 g was chosen and Knoop indentations were performed in series starting from the external coating surface down to the substrate, at constant spacing of 30 µm (about 2,5 times the length of the short diagonal – see figure 2).

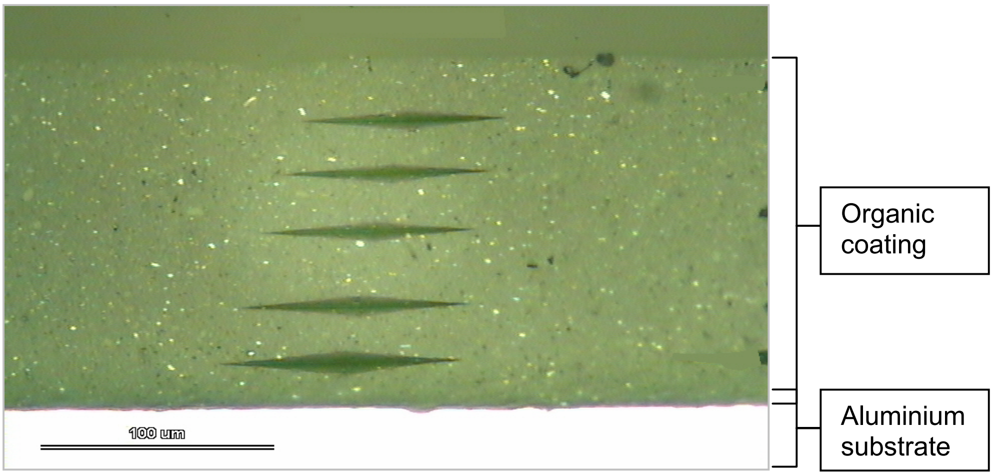

Figure 2. Series of micro-indentations on a cross-section of paint layer, showing a lower hardness near the aluminium substrate

The results concerning with the three curing conditions for low and high thickness test panels are shown respectively in figure 3 and 4, as a function of the impression distance from the external coating surface.

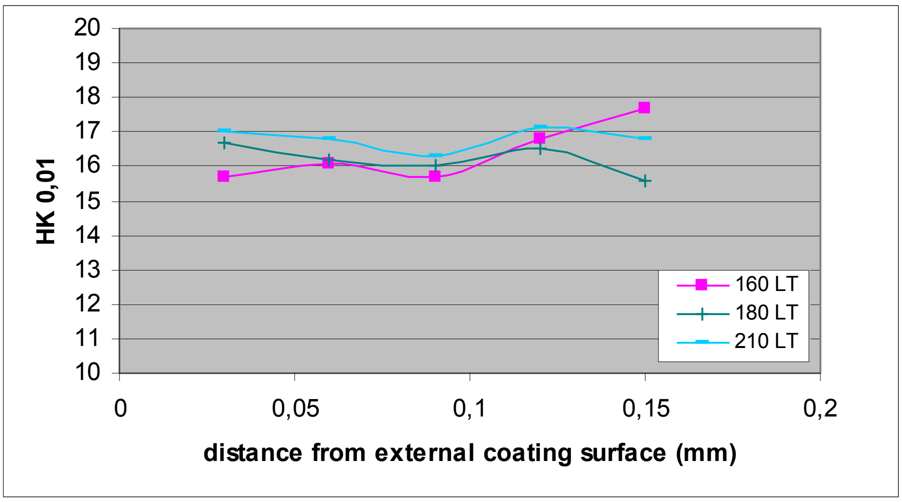

Figure 3. Micro–hardness measured on a cross-section of paint layers
Low thickness test panels

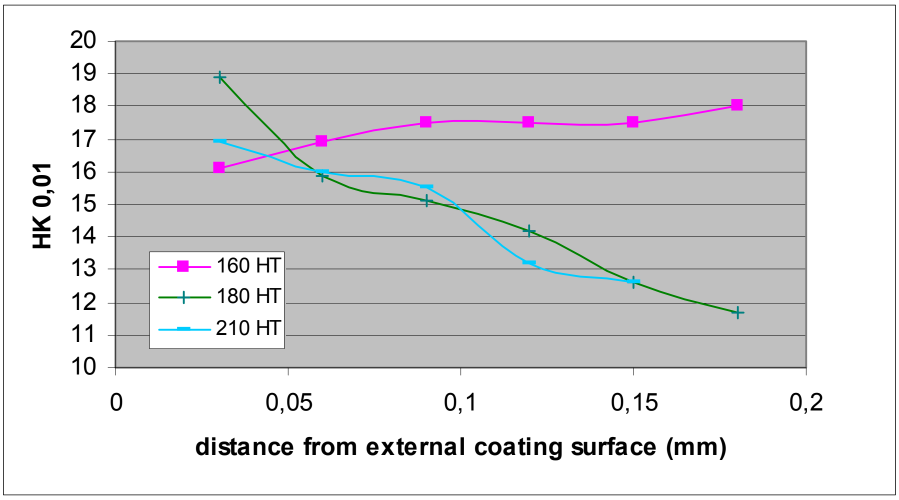

**Figure 4. Micro–hardness measured on a cross-section of paint layers
High thickness test panels**

Results

Focusing our attention on the micro-hardness results obtained trough the cross section of paint layers, it was noticed that:

- at the curing condition of 180°C x 20 min (recommended condition), the coating exhibits hardness values substantially uniform in the whole layer, but only for low thickness test panels; in the case of higher thickness, instead, the hardness values throughout the layer gradually decrease from about 19 HK (near the external coating surface) to 12 HK (near the metal surface);
- at the curing condition of 210°C x 20 min (overbaked condition), the coating hardness shows the same behaviour observed for the samples cured at 180°C x 20 min, both in the case of low and high thickness test panels;
- at the curing condition of 160°C x 10 min (underbaked condition), the coating hardness has an opposite trend both for low and high thickness test panels, in fact the values grow from about 15 HK (near the external coating surface) to 18 HK (near the metal surface).

Taking into account the impact test results (meaningful of the coating curing), the layer is able to withstand the highest energy values when the coating is cured at recommended temperature/time condition or above (at least in the range of temperature investigated) that is, when the whole layer shows a constant indentation resistance. But the behaviour changes with the increasing of the layer thickness; in fact at higher thickness the layer is not able to achieve the highest energy values in the impact test and it was seen to become softer near the aluminium substrate. Finally, when the coating is underbaked (in the whole range of thickness evaluated) the layer withstands a very low impact energy (0,3 Joule) and it was seen to become harder near the aluminium substrate.

In conclusion, the micro-hardness measurements performed on the cross-section of painted layers have been demonstrated as a useful procedure for a deeper characterization of the organic coating and the data obtained are in good agreement with impact test results. The other tests performed, involving only the surface properties of the organic coating, are not directly comparable with cross section hardness results.
This field of investigation is practically new and quite complex. Future work should involve extensive test programs to complete the analysis of all the factors influencing organic coating properties.