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The quantitative determination of chalking

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1 Definition

The term chalking refers to the formation of a loosely adhered chalky powder on the surface of a film or coat arising from the degradation of one or more of its constituents. In most cases it is caused by the photocatalytic properties of titanium dioxide (TiO_2) which is used in the majority of paint formulations.

An example for chalking on a car: car wing (left) affected by chalking compared with a new door (right) (Wikipedia)

The phenomenon occurs after exposure of the coated surface to weathering. The contained titanium dioxide absorbs UV light converting the TiO_2 into a chemically highly reactive state. This causes degradation of the organic materials in which the TiO_2 is embedded. Pigments and fillers are exposed at the surface and this leads to the typical whitish-matt appearance of chalked paint surfaces.

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1.1 Motivation

While the photoinduced semiconductor properties of TiO_2 are a desired effect in several applications, like for example, in the construction of materials with self cleaning properties, it is generally highly undesirable in coatings as it has detrimental effects.

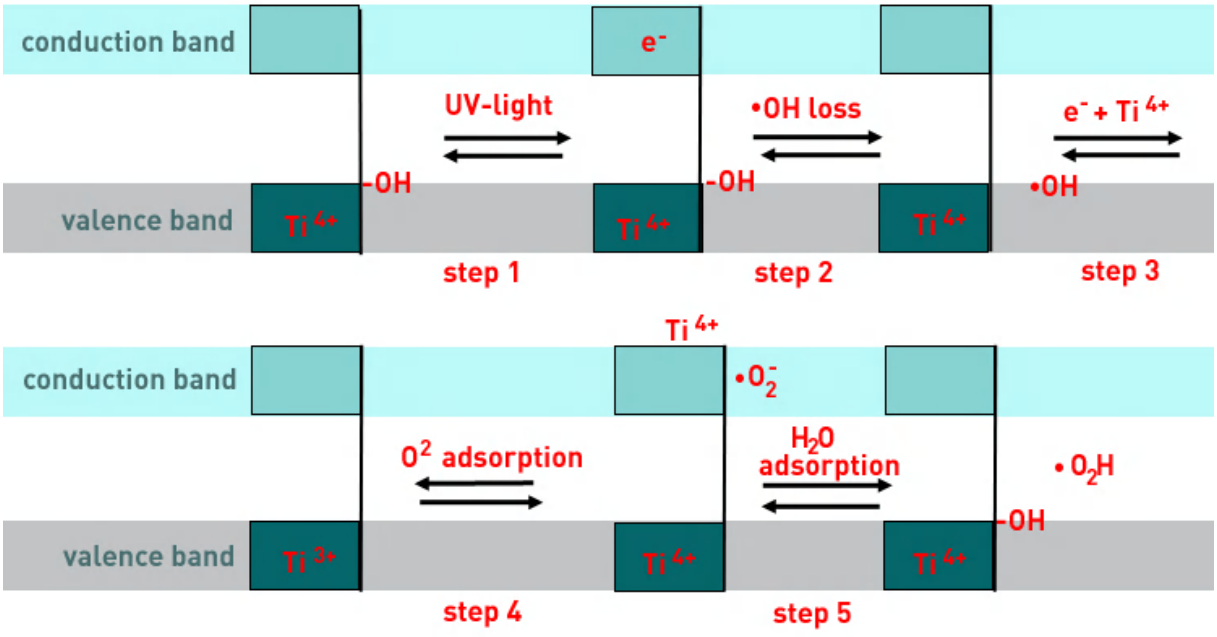
Chalking can bleed out to the substrate (e.g. brickwork) and deface the appearance of the surface; it can alter the optical appearance by lightening the colour of the coating and it can erode the coating film due to mass loss resulting in a loss of protection of the substrate.

Therefore the chalking properties of a coating are an important factor to be studied in natural and artificial weathering tests and it is important to have a method at hand for the reliable and reproducible quantitative determination.

1.2 Chalking cycle of titanium dioxide

The absorption of UV light by TiO_2 hoists binding electrons from the valence band into the conduction band, leaving a positively charged "hole" in the valence band.

This triggers a 5-step-reaction, the so called chalking cycle, eventually resulting in the formation of two radicals: one hydroxyl radical and one hydroperoxide radical.



Chalking cycle of Titanium Dioxide; adapted from: Winkler, 2003

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It also becomes obvious that not only ultraviolet radiation but also the presence of oxygen and water is required to complete the full chalking cycle – the classic conditions of outdoor weathering.

The resulting radicals trigger degradation processes in the embedding polymeric materials. Pigment and binder particles migrate to the surface of the paint. They are no longer embedded in the polymeric matrix and can be wiped off easily. Underneath the chalking layer the original hue of the paint will reappear.

This loose pigment layer changes the optical appearance of the paint: due to the rougher surface, the gloss is reduced and the changed reflective properties (higher diffusion) lead to a matt whitish appearance.

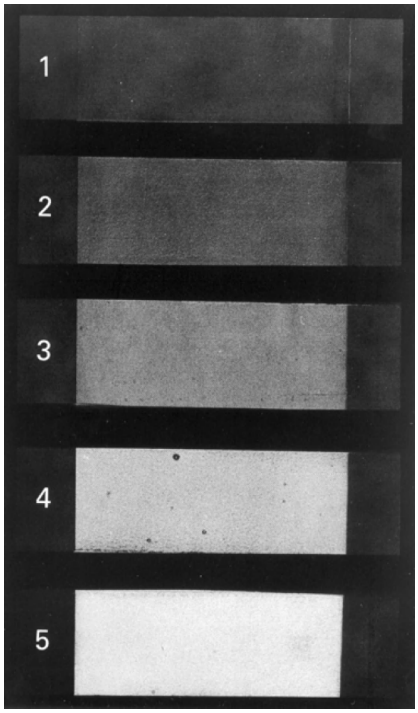
2 Common methods for the quantitative determination of chalking

For many decades a variety of methods for the determination of chalking have been in use which are significantly different in handling and reliability.

In this paper the methods will be contrasted and compared with special focus on their practicability and the reliability of the results. The results of a comparative scientific survey of these methods will be presented.

2.1 Tape method according to ISO 4628-6 (formerly DIN 53223)

Chalking is taken off the surface under inspection with adhesive tape and later evaluated visually by comparing it with pictorial reference standards as shown in the standard.



Pictorial reference standards for numerical chalking ratings 1 to 5 (ISO 4628-6)

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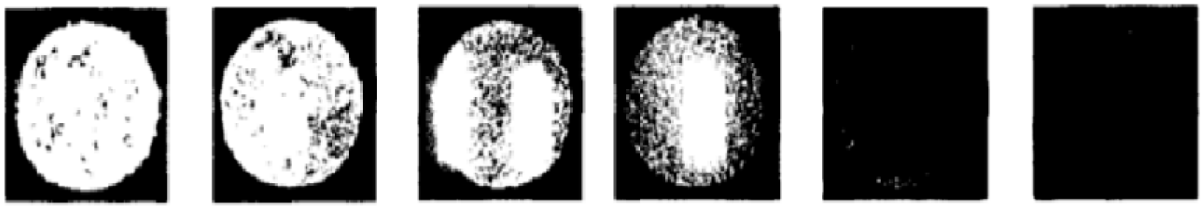
2.2 Kempf method according to DIN 53159

The Kempf method uses the gelatine side of photographic paper to pick up chalking particles. A specially designed stamp is used to exert a repeatable force. Similar to the tape method used in ISO 4628-6, the results are evaluated either according to a relative assessment scale in accordance with ISO 4628-1 or visually compared with a reference standard.



Pictorial reference standard for evaluation of the amount of chalking according to Kempf (example)

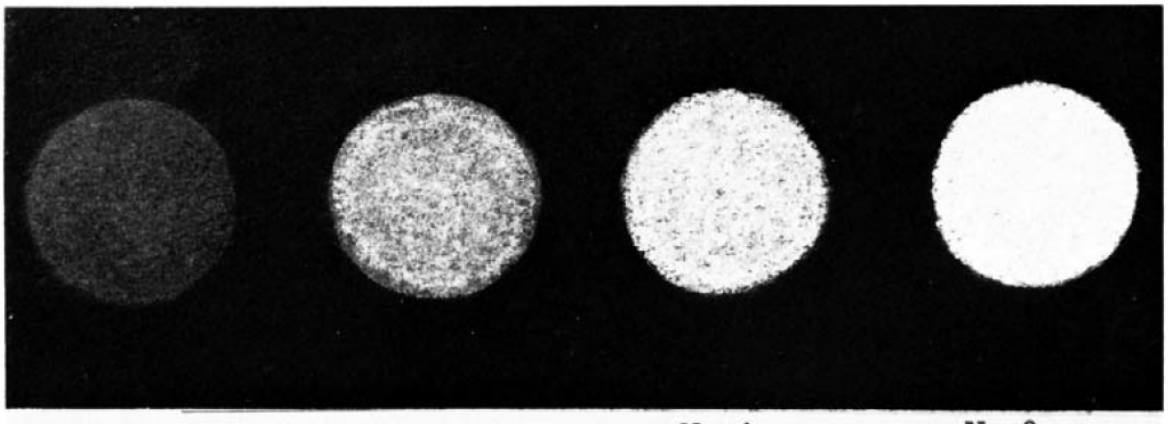
Since the success of digital photography the availability of photographic paper is decreasing and it is becoming more and more expensive.

2.3 Other methods according to ASTM D4214

Additionally to the above mentioned methods, ASTM D4214 lists:

2.3.1 Cloth tape method (formerly ASTM D659)

Chalking is rubbed off by wrapping a black cloth around the index finger. Visual evaluation by comparing with photographic reference standard No. 1 as pictured in the standard.



Photographic Reference Standard No. 1
Test Method D659 (ASTM D4214)

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2.3.2 Wet finger method

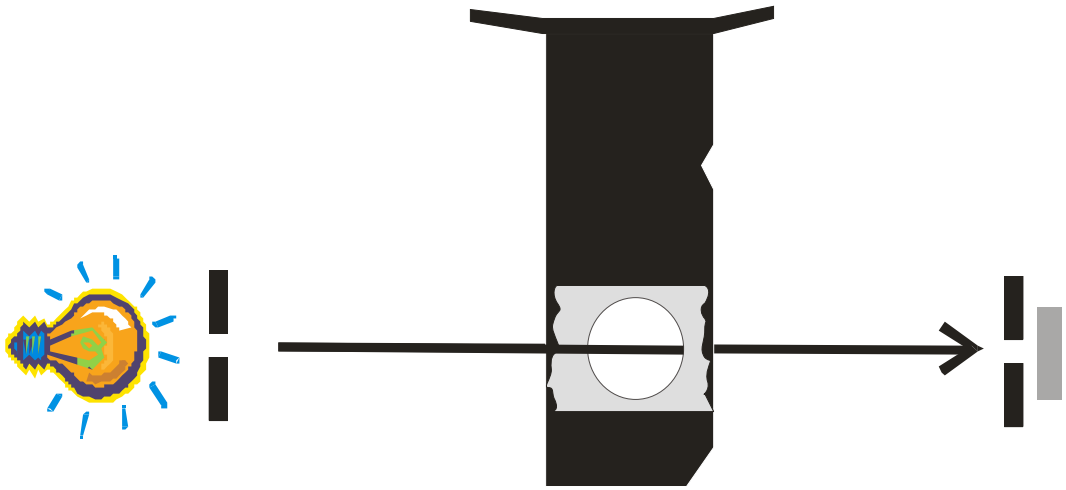
Chalking is rubbed off with a moistened fingertip and rated as None, Visible or Severe. (ASTM D4214)

Due to the imprecise description of the testing and evaluation procedure and the resulting bad reproducibility, this method will not be considered further in this context.

2.4 Helmen method (EN 13523-14)

This is a combination between the Tape method and an objective measuring method based on the principle of nephelometry. Similar to the tape method, chalking is taken off the surface under inspection with a specified adhesive tape. The quantity of chalking is then determined with an electronic measuring instrument. Thus the factors influenced by the operator which can lead to differing results are minimized.

A piece of transparent adhesive tape is placed on the testing surface and rubbed on with a plastic spatula or with the fingers until it adheres to the surface optimally. The tape is removed and its transparency is measured.



Principle of chalking measurement according to EN 13523-14

For this measurement two types of instruments can be used: either a specially designed chalking tester which will directly display the relative chalking in percent or a transmissions instrument by means of which the indicated value can be converted into relative chalking by the following formula

x % transmission = (100 - x) % relative chalking

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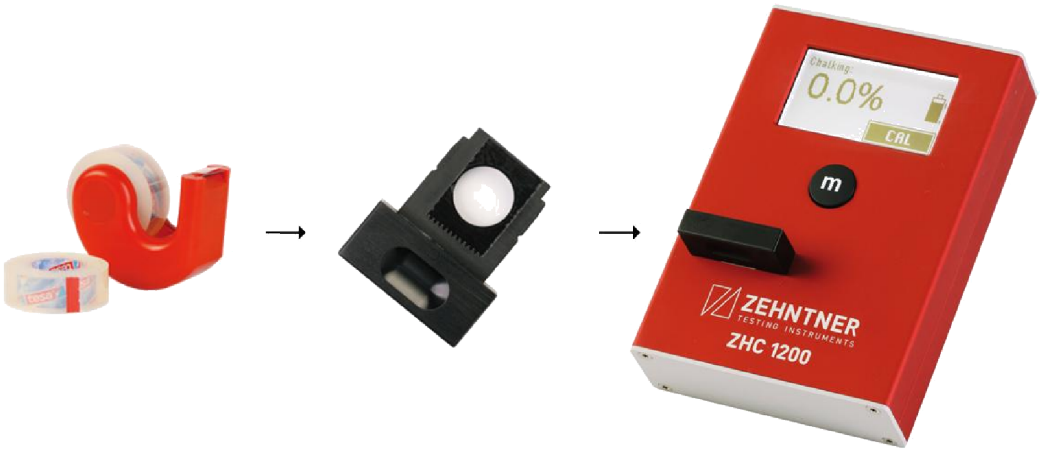
For calibration the transmission of the blank tape has to be excluded. Therefore a piece of blank transparent adhesive tape is placed on the sample holder and inserted in the instrument. The degree of chalking is set to zero.



Calibration of chalking tester (Zehntner ZHC 1200)

For measurement a piece of adhesive type of the same type is placed on the testing surface and rubbed on with a plastic spatula or with the fingers until it adheres to the surface optimally.

Transferring chalking particles to adhesive tape

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The tape is removed and put on the sample holder. Its transparency is measured and the degree of chalking is calculated and displayed directly on the instrument.

Determination of chalking with chalking tester (Zehntner ZHC 1200)

3 Comparative Study (Helmen, 1978)

3.1 Sample population

As early as 1978 a comparative study between the different methods has been conducted by T. Helmen et.al. Even though the results have clearly shown that some methods are unreliable and dependent on the operator, they are still in use until today. For this paper data gathered by Helmen have been reassembled and evaluated with focus on the comparability of the individual methods.

A series of lacquers of different colours have been weathered for this study with the aim of producing samples with a wide range of chalkiness from very little up to high degrees of chalking. Out of these samples a total of 880 chalking tests have been carried out.

Sample colour	Samples	Chalking degrees
white	11	6
light gray	4	1
dark gray	4	4
black	1	1
blue	4	1
red	3	3

Composition of the sample population (Helmen, 1978)

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3.2 Probands

In the survey, the above mentioned 4 methods have been carried out by four people and the results are compared to each other.

3.3 Results

The following pictures show the comparison of the 4 different methods Helmen, tape, Kempf and tissue each on the same chalking samples. For better comparison, the data have been normalized to 100%:

For the Helmen method the values appear as indicated on the measuring instrument.

Tape method: the method divides the degree of chalking into 5 steps, 5 meaning very high degree of chalking and 1 meaning low chalking. These ratings have been converted into percentage:

Tape (ISO 4628-6)	
Rating	Percentage
1	20 %
2	40 %
3	60 %
4	80 %
5	100 %

The Kempf method (6 steps) and tissue method (5 steps) have also been converted accordingly:

Kempf (DIN 53159)	
Rating	Percentage
1	16.67 %
2	33.33 %
3	50.00 %
4	66.67 %
5	83.33 %
6	100.0 %

Tissue (ASTM D4214)	
Rating	Percentage
1	20 %
2	40 %
3	60 %
4	80 %
5	100 %

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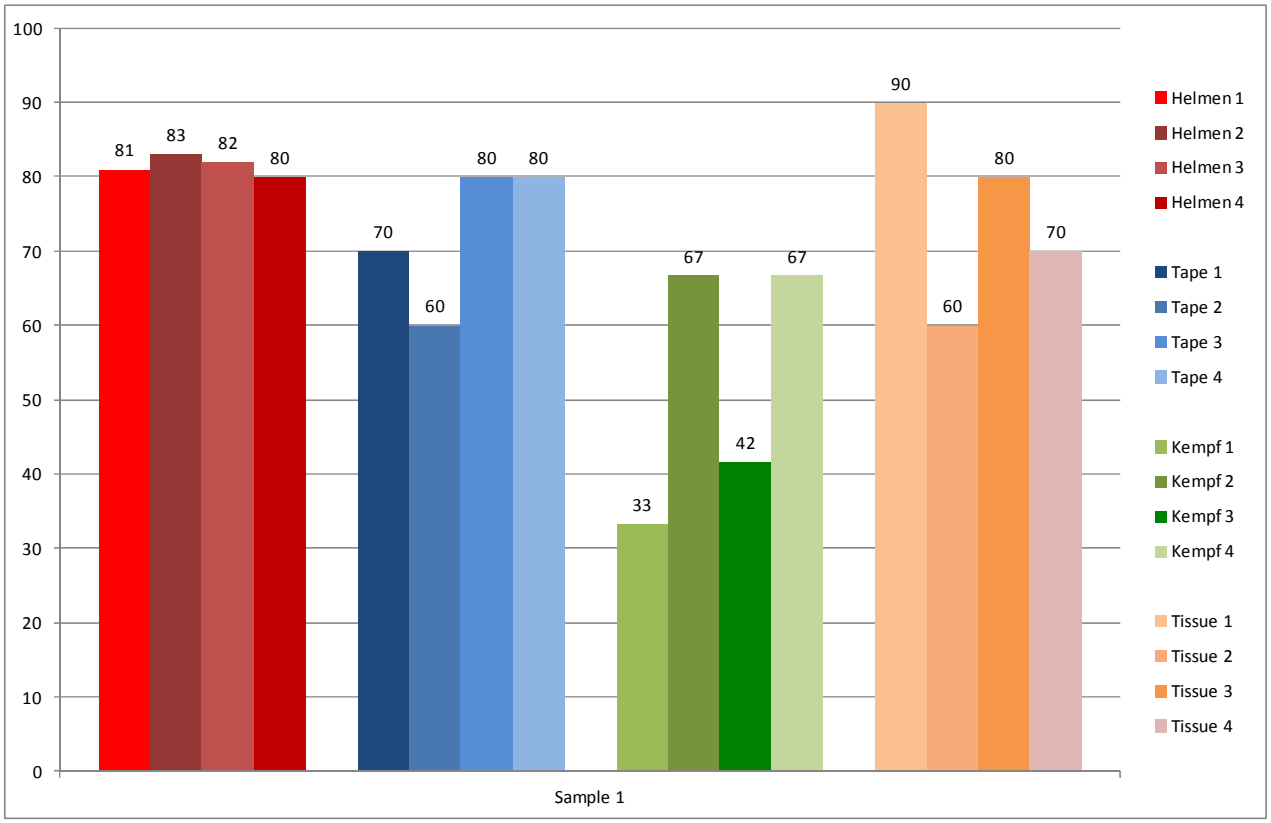

Comparison of different methods of determining the degree of chalking. Adapted from: Helmen, 1978

The results for the other samples show a similar pattern. Obviously the Helmen method and within limitations also the tape method show the best reproducibility whereas the results of the Kempf method and the tissue method are highly dependent on the operator.

For a more detailed analysis of the 2 methods using adhesive tape (Helmen method and tape method), a precise quantitative determination of the TiO_2-content has been carried out with atomic absorption spectroscopy (AAS). For this analysis, 1 cm^2 of each of the tapes containing the chalking imprints has been punched out and the TiO_2 has been dissolved and determined with AAS.

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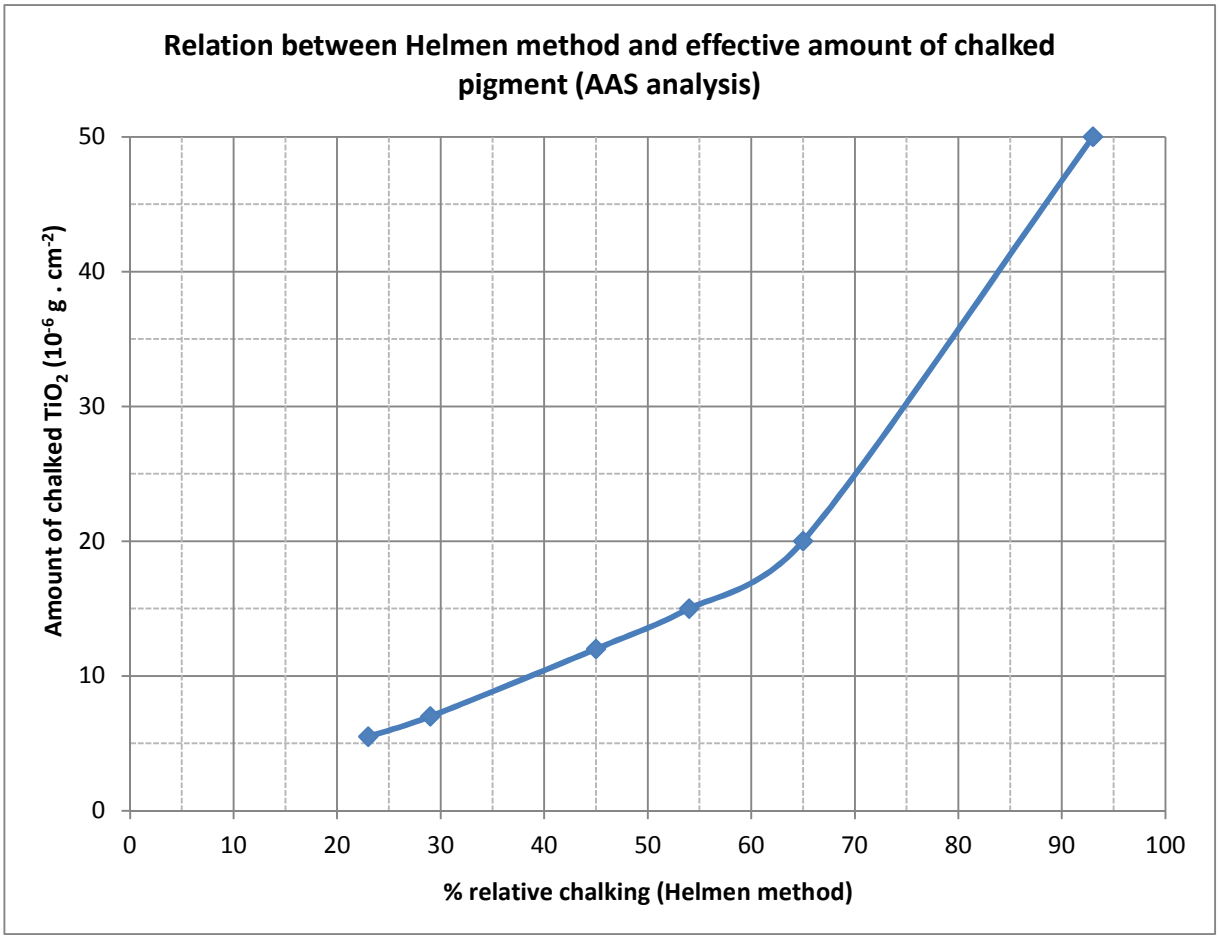

Relation between Helmen method and effective amount of chalked pigment (AAS analysis) (Helmen, 1978)

The graph shows that there is an almost linear correlation between the effective amount of chalked pigment and the measurement results up to 60-70% relative chalking. Thus, this method is highly suitable especially for the most important early stages of chalking.

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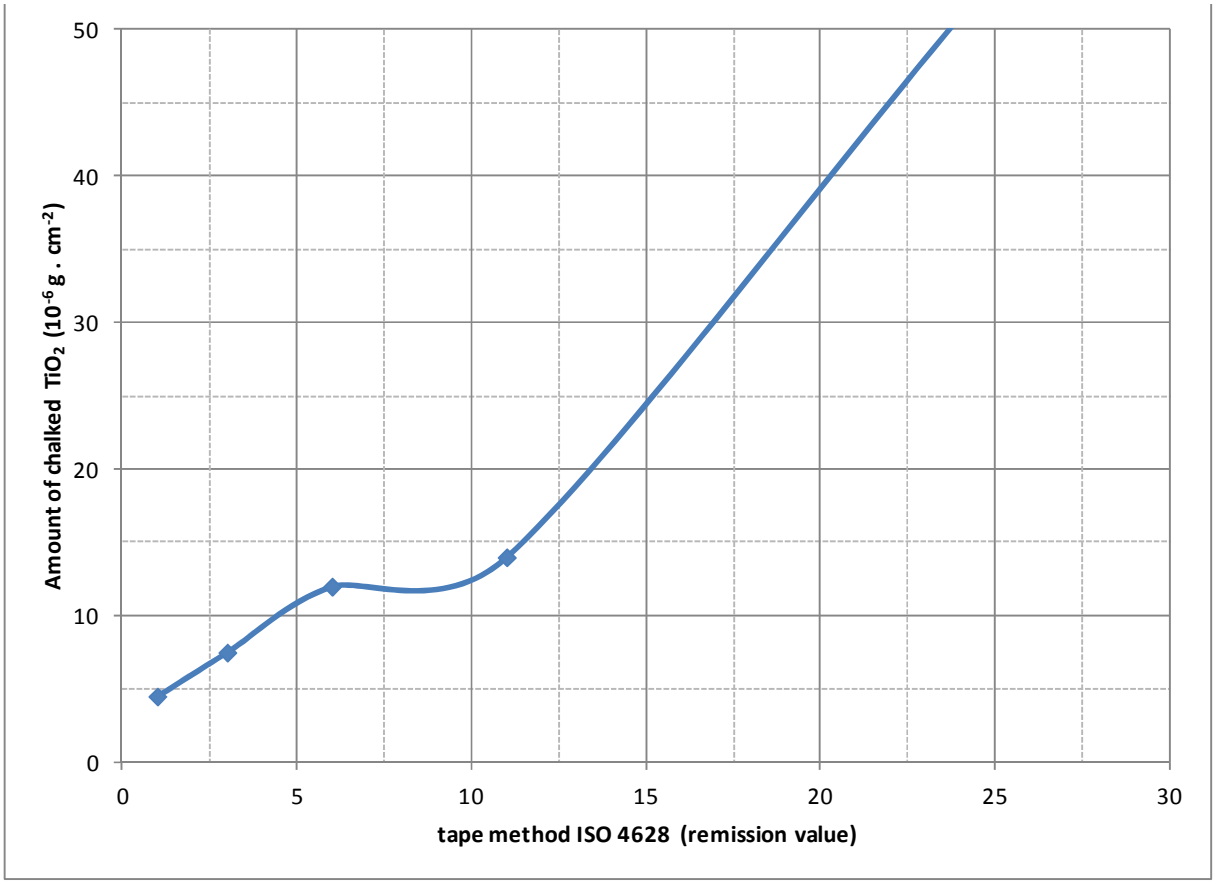

Relation between tape method (ISO 4628-6) and effective amount of chalked pigment (AAS analysis) (Helmen, 1978)

To exclude the operator-caused differences, remission measurement has been carried out on the samples that have been taken with the tape method. Even then, the correlation for this method is less favourable than the correlation for the Helmen method, especially in the important early stages of chalking.

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4 Conclusion

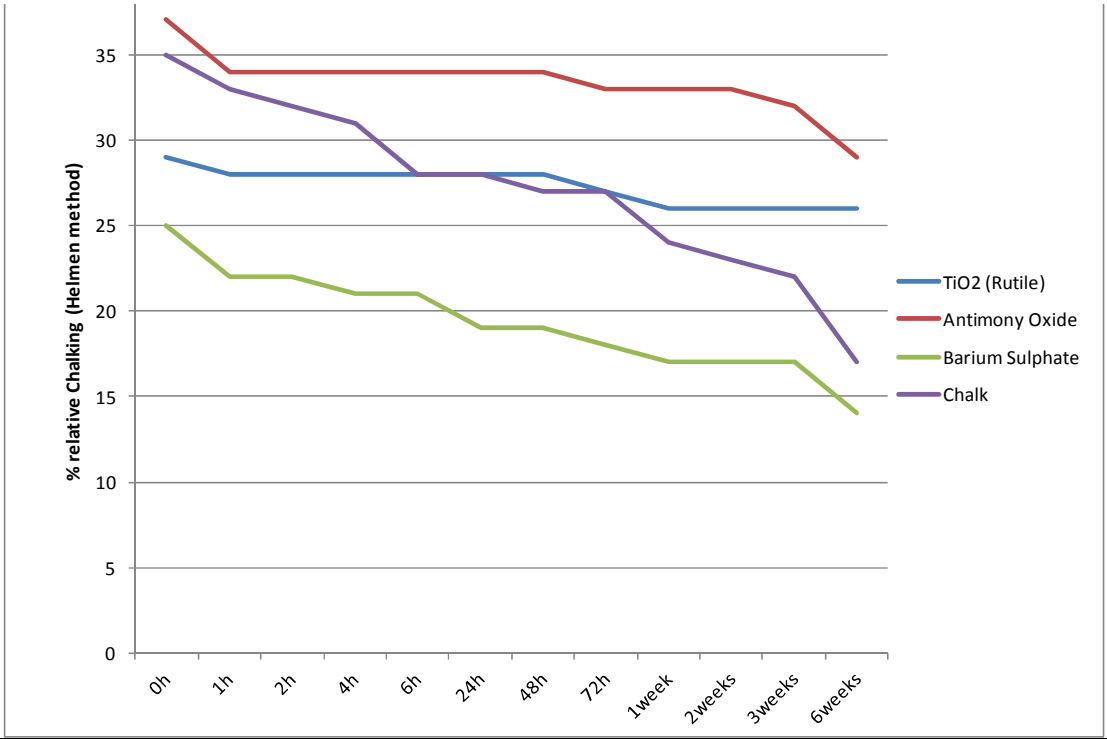
The method according to Helmen is the most reliable and reproducible method to determine the amount of chalking of coatings. The results of all other methods vary strongly depending on the person who executes the test. If an objective statement about chalking is needed it is highly recommended to use the Helmen method. For many years, practical experience has shown that it is the easiest and fastest method which can be used in the laboratory as well as directly at an outdoor weathering site.

At the ECS 2013 Zehntner is presenting a new chalking measuring device working with the Helmen method, the ZHC 1200 HELMEN®-Chalking tester which gives a direct reading of the relative degree of chalking in percent.

5 Practical application

5.1 Influence of storage time of tape samples

With either method it is recommendable to make the measurement or assessment immediately after taking the sample. While the titanium dioxide content of the sample remains relatively stable over time, the amount of other chalking agents like antimony oxide, barium sulphate or chalk will gradually degrade.



percental decrease of chalking after 6 weeks of sample storage	TiO_2 (Rutile)	Antimony Oxide	Barium Sulphate	Chalk
	-10.30%	-21.60%	-44%	-51.40%

Time based change of the tape print composition, measured with the Helmen method (Helmen, 1978)

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5.1.1 Influence of tape quality and temperature

As it is to be expected that the adhesive strength of the tape will have an influence on the test results, a specific tape is required in the standards. Nonetheless, it is recommended to conduct a simple test when changing the brand or type of adhesive tape.

For higher degrees of chalking the adhesive quality of the tape does not have a large impact on the testing results. For lower chalking however, it is recommended to make a "zero" test on a glossy unweathered sample. If this test will show 10 or more percent of relative chalking, the tape is unsuitable for chalking testing and should not be used.

The ambient temperature and temperatures of the sample and the tape have not shown a considerable influence on the results, so the test can also be carried out directly on outdoor weathering sites without concern for temperature influence.

6 Literature

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