

Studying and preventing leaching of façade paints: Method developments Novel additive can aid the formulator to decrease leaching of dispersing agent

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RESULTS AT A GLANCE

- **Leaching of façade paints can significantly deteriorate the paint's optical appearance by emergence of so-called "snail trails."**
- **To date, prediction of a paint formulation's tendency towards leaching is difficult, because the phenomenon is poorly understood and no standardized methods exist to study and deepen the understanding.**
- **Two novel test methods help to investigate leaching both from an optical appearance aspect and for identifying the leached ingredients.**
- **The semi-quantitative analytical approach is exemplified by the study of a surfactant-type and a novel polymeric dispersant.**

Leaching of façade paint can occur when water condenses on freshly-dried painted walls, leaving behind shiny vertical "snail trails" that alter and deteriorate the façade's optical appearance. A newly developed test method can mimic leaching conditions and thus help to study the influence of paint ingredients on the occurrence of snail trails. In addition, a new polymeric dispersant that is resistant to leaching was devised to aid the formulator in his selection choice.

Freshly painted façades are still accessible to weather influences, particularly in spring or autumn, when temperatures fall below the dew point more easily.[1] The latex paint's film curing process is retarded under these conditions, thus making the paint susceptible to the humidity influence. As long as the binder film has not sealed the paint surface completely, condensed water can mobilize water-soluble paint ingredients, which then migrate to the surface. As the condensed water evaporates, the concentrated residues appear as stains, gloss patterns or snail trails. It is still not fully understood which ingredients are extracted, but surfactants are suspected to be a main contributor, due to their water solubility and mobility. They are introduced into the initial paint formulation via binders, pigment paste, as wetting agents and emulsifiers. Formulating a paint without surfactants, however, is a futile endeavor, since they have essential functions in the paint manufacture and application process.

The impact can be seen on dark shades in particular: The tinting colorants can introduce high amounts of water soluble ingredients. Even if a white paint has been optimized, all the benefits can be annihilated by the tinting. The shiny snail trails are in strong contrast to the somber complexion of the rest of the façade. The consequence are customer claims and, in the worst case, the façade has to be repainted, leading to compensation costs for the paint manufacturer. On white paint, on the other hand, the snail trails can become visible when microorganisms or dirt stick to them, thus giving them a dark appearance. This defect is termed dirt pick-up.[2]

NOVEL TEST METHODS AID TO TACKLE DOWN THE SOURCE OF THE SNAIL TRAILS

In order to gain deeper insight into the source of the snail trails rather than speculating, we intended to develop methods that can investigate the phenomenon in qualitative and semi-quantitative manner. The methods that have been published to date mainly focus on the binder itself^[3] or the environmental impact.^[4] The ASTM norm D7190-10 (2015) to study surfactant leaching only gives an optical rating resulting from water droplets sitting on the paint film.^[5]

A qualitative test should allow to screen paint formulations and quickly exclude those that leach. The semi-quantitative test should, by comparison to standards, identify the responsible ingredient. By head-to-head comparison, two types of ingredients can be quantified.

QUALITATIVE TEST - DOES THE PAINT FORMULATION DEVELOP SNAIL TRAILS?

For the qualitative analysis, a conventional Kesternich cabinet can be used easily.

The paint of interest is applied on black Leneta Scrub Test panels (poly-vinylchloride/acetate copolymer; according to DIN 53778) as a substrate. The paint is applied in 400µm wet film thickness (corresponding to approximately two layers paint film on a façade), leaving 3-4 cm blank at both short ends of the panel. After drying, one panel is cut into two halves in order to run the test in duplicates. The remaining blank end of each panel can be used to form “pockets” using Scotch tape, so that the leached eluate that runs down the painted surface can be collected (see Figure 1). The flexibility of the foil also allows for punching holes. The punched holes serve as a tool to hang the foil into the Kesternich cabinet vertically, thus mimicking the orientation of the façade. In addition, tailor-made hooks ensure that the painted surface points outwards towards the glass walls of the Kesternich chamber, so that they are exposed to plenty of water.

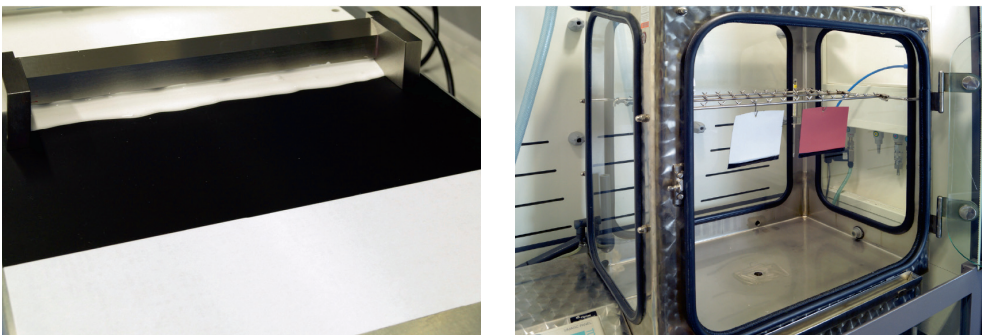


Figure 1: Preparing the foil and foil including pockets in Kesternich chamber

After submission to warm water vapour according to the “Schwitzwassertest” (DIN 50017), the paint surface can be evaluated after a thorough drying time. Particularly on tinted paint, the presence of snail trails can quickly be determined. Furthermore, they can be visualized in higher magnification with the aid of a hand-held microscope (see Figure 2). In addition to the paint surface, the pockets, in which condensed water can be collected, serve as indicator for leaching. After drying, the presence of residue hints at very water-soluble leached ingredients that may not be visible on the small area of the panel, yet may cause a problem on a tall façade. In our standard test, foils were inserted in the Kesternich chamber in duplicates. Thus, three paint samples can be studied at a time. This Kesternich cabinet test serves as a good screening method for various paint formulations.

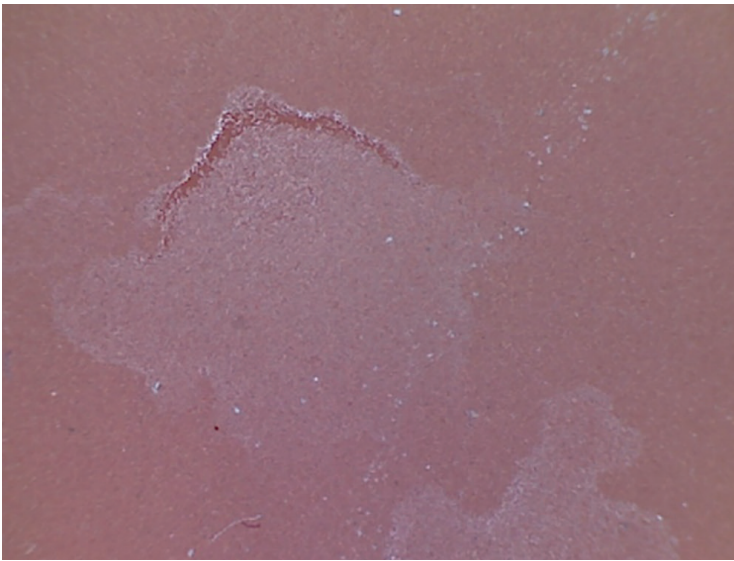


Figure 2: Microscope image of a snail trail on the surface of the panel

ILLUSTRATING THE PRACTICAL USE OF THE TEST: VARIOUS BINDERS IN A PAINT FORMULATION

As a proof-of-concept, we investigated a highly simplified white paint formulation for the impact of various binders. The paint formulation was fabricated as one batch of slurry that was then split into batches that were mixed with different binders, in order to avoid weighing errors of the other ingredients. Some ingredients that are also suspected to leach were deliberately left out: The paint formulation does not include defoamer, nor additional rheology modifiers after the grinding step (hydrophobically modified alkali swellable emulsion (HASE) thickener). The wetting agent was reduced to the minimum amount necessary for grinding Titanium dioxide and fillers.

Different monomer compositions in the binder and different minimum film temperatures were evaluated (see Tables 1 and 2 for paint formulation and binders). In a challenging high PVC paint, different results were obtained. Binders 3 and 4 showed almost no snail trails and clean pockets, while Binders 1 and 2 clearly exhibited shiny marks on the paint surface and residues in the pocket (Figure 3). This means that Binders 1 and 2 should be increased in their amounts in order to seal the paint surface better and obtain similar results to Binders 3 and 4, which already function even at high PVC formulation. Due to the higher MFT for Binders 1 and 2, a coalescing agent may be necessary for a better performance.

Table 1: Simplified paint formulation for leaching

INGREDIENT	m-%
Water	28.20
Thickener	0.50
Wetting agent (polyacrylate)	0,10
Titanium dioxide	10.00
Mixture of fillers (CaCO ₃ , Talcum, Kaolin)	39.00
Biocide (MIT + BIT)	0.20
Binder to be investigated	22.00

Table 2: Binders that were studied in the qualitative test

BINDER NAME	MONOMER COMPOSITION	MFT (minimum film forming temperature)
Binder 1	pure acrylic	19°C
Binder 2	pure acrylic	15°C
Binder 3	pure acrylic	1°C
Binder 4	Veova-acrylic	10°C



Figure 3: Images of Binder 2, showing film-forming residue in the pocket, shiny snail trails per microscope, and shiny still trails on the foil surface.

QUANTITATIVE TEST: TACKLING THE ROOT-CAUSE OF A LEACHING PAINT

While the Kesternich cabinet test helps to judge whether a paint formulation is prone to leaching, it does not reveal which ingredient of the formulation is the culprit for the snail trails in a more complex paint formulation. In order to answer this question, a more sophisticated test is needed and adjustments have to be made. For a known paint formulation, those ingredients that are suspected to be a contributor are analyzed for their retention time via liquid chromatography (high performance liquid chromatography (HPLC): small molecules; or gel permeation chromatography (GPC): polymers). The paint formulation is applied to the back side of ceramic tiles (bathroom tiles) as mineral substrate. The paint is applied with a foam roller brush and the weight of the paint is recorded. About 11 g wet paint per tile (ca. 14 x 14 cm) are desirable (corresponds roughly to the layer thickness of 400 μm on the panels that were used for the Kesternich test).

The Kesternich cabinet is exchanged for a modified aquarium with a cold water vapour condenser attached to it (Figure 4). The cold water serves as a comparison of the real leaching conditions in the morning dew of spring or autumn.



Figure 4: Modified aquarium with a cold water vapour condenser attached to it to study leaching

In the modified aquarium, four tiles can be studied at a time. When working with duplicates, this means that two paint formulations can be investigated simultaneously. Each tile is erected using a metal holder that stands in a flat glass basin. The eluate is collected in the glass basin. At the end of the “leaching cycle”, the water from the glass basin is weighed and then concentrated to compensate for the detection limits of the HPLC. After injection into the measuring device, the retention time of any peak occurring can be compared to the standards that were measured before. This allows to find the leached paint ingredient or ingredients. The test itself is more cumbersome than the mere visual evaluation by the Kesternich test. Nevertheless, it is very valuable whenever the root-cause of the leaching shall be identified.

In a semi-quantitative fashion, amounts of leached components can be compared relative to each other. Weighing errors can occur during the transfers of eluates or sample concentration. In addition, the amount of the paint on the tile can vary slightly, plus there are additional weighing errors when determining the wet and the dry paint. All these slight variations lead us to the conclusion that a completely quantitative evaluation is not possible. It also may not be required for the time being, as the root cause study of snail trails in various paint formulations has just begun.

CASE STUDY: DISPERSING AGENT

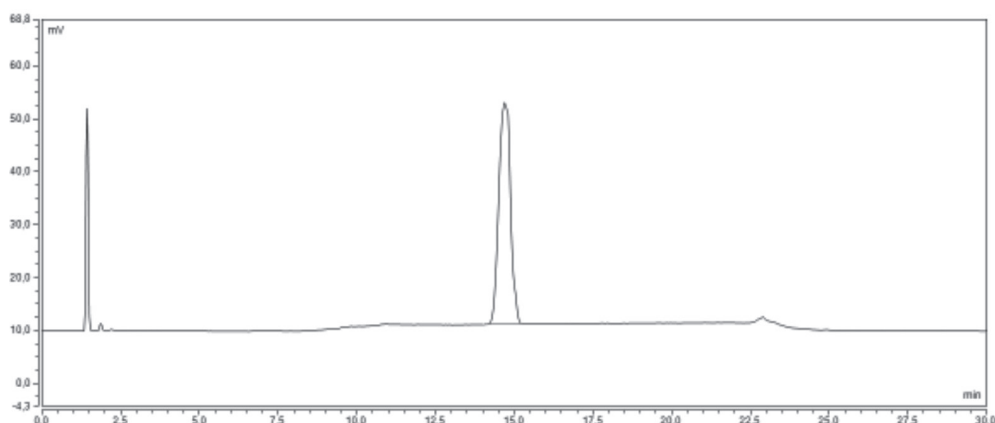
A paint component that is present in the (tinted) paint in an amount that can lead to optical deterioration of a façade when leached out is the dispersing agent. We thus developed a novel polymeric dispersing agent. In theory, a polymeric dispersing agent is less mobile in the paint formulation due to slower Brownian motion and entanglement of the polymer chains with other paint ingredients. In order to study this effect, a pigment paste featuring the new polymeric dispersing agent and a comparative paste featuring a conventional surfactant-type dispersing agent were fabricated. Both pastes were used to tint the same white base paint. As a pigment, we chose an iron oxide red (PR 101), because snail trails are more visible on darker shades and inorganic pigments are frequently used on exterior walls. The pigment paste formulation is shown in Table 3. Again, it is simplified as much as possible in order to avoid the influence of other ingredients. 8% of this pigment paste were used to tint the base paint.

Table 3: Pigment paste formulation

INGREDIENT	m-%
Defoamer	0.3
Biocide	0.2
Dispersing agent	4.0
Pigment Red 101 (Bayferrox 130 M)	65.0
Water	ad 100

The optical evaluation with the Kesternich cabinet test revealed shiny snail trails on the smooth pigment surface for the paint that had been formulated with the surfactant-type dispersing agent. The paint formulated with the novel polymer, however, remained unaltered even after being subjected to the test. In order to quantify the amount of leached ingredient, we also ran the aquarium test with tiles as a substrate.

HPLC trace of the surfactant-type dispersant as standard



HPLC trace of the leached eluate, using the same method. The peak at about 15 min retention time clearly indicates the presence of the surfactant.

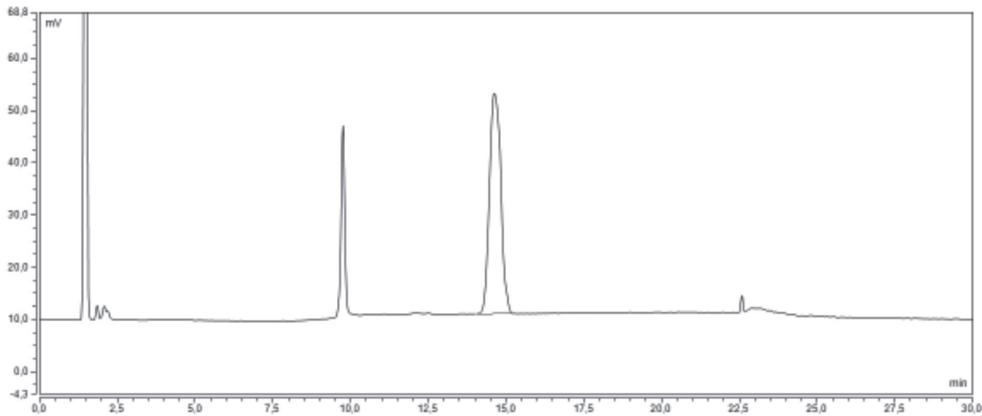


Figure 5: HPLC traces of the surfactant type dispersant as standard versus in the paint

Standards of the two dispersing agents were used for the method development via liquid chromatography. As can be seen from Figure 5, the surfactant has a retention time of 15 minutes on the HPLC elugram. The polymer, on the other hand, need to be detected via gel permeation chromatography, due to the higher molecular weight. Its retention time was ca. 20 minutes. When injecting the eluate of the corresponding glass basin into an HPLC device, a large peak with retention time 15 minutes could be found for the surfactant that leached off the tile. The eluate from the tile featuring the polymeric dispersing agent, on the other hand, only revealed a small peak. Using the area under the curves and comparing to a calibration curve, a very rough quantification of the leached dispersing agents was achieved. For the surfactant-type dispersing agent, roughly 2,1 g/L were found, while for the polymer, only 0,4 g/L were detected. These numbers shall not be taken as absolute numbers, but can be seen relative to each other. When setting these numbers into ratio, it becomes obvious that the polymeric dispersing agent is washed out five times less than the surfactant-type dispersing agent.



WRAP-UP

In summary, two novel methods that help to predict the propensity of a paint for leaching were developed in our laboratories. A qualitative test in a Kesternich cabinet serves for visualization of snail trails in any paint formulation, while a semi-quantitative test in a modified aquarium can identify the responsible ingredient. In parallel, a new polymeric dispersing agent can minimize leaching of dispersing agents in finished paint formulations.

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