Leather topcoats with anti-soiling and non-squeak properties

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In the last few years upholstery and automotive interior designers have increasingly selected leathers in light colours such as white, beige or grey. At the same time, they have chosen to use more leathers with a very high degree of matting. These leathers provide the modern and elegant look designers strive for.

But these leathers are a concern for the quality departments of manufacturers. Very often, the pristine look in the showroom is lost due to soiling of the leather surfaces. It can be said that today soiling is among the main reasons for claims regarding upholstery and automotive leather.

Another property of leather receiving little attention has also become much more important during the last few years, especially in the automotive sector. Due to the significant progress made regarding the reduction of noise by car manufacturers, the noise created by an uneven movement when two surfaces are rubbed against each other is now recognizable and perceived as obtrusive. Leather has the tendency to produce this effect, but it can be measured by the so-called 'Stick-Slip' test.

Leather manufacturers, and with them chemical suppliers, therefore face the challenge to provide leathers which have and maintain these aesthetic and technical properties over a long period of time, preferably the whole lifespan of the article.

The requirements of anti-soiling systems

Leathers finished with a conventional coating system - using either silica or organic matting agents - do not answer the demand for articles with low soiling properties. Solutions are needed to address these new technical requirements.

These solutions also need to take into account the economic and practical needs of leather manufacturers. In this context, one of the biggest concerns regarding low-soiling coating systems has been the possibility to apply corrective coatings in order to adjust the final shade of the article. The requirements for an efficient and versatile anti-soiling coating system can therefore be summarised as follows:

- Significantly reduced tendency for soiling.
- Easy removal of any dirt that is still accumulating ("easy-clean effect").
- The permanence of the anti-soiling effect.
- Re-coatability for adjustment of final shade.
- High degree of matting.
- Similar touch/feel to conventional coating systems.
- Equal or better physical properties than conventional systems.
- Excellent Stick-Slip performance (mainly for automotive leathers).

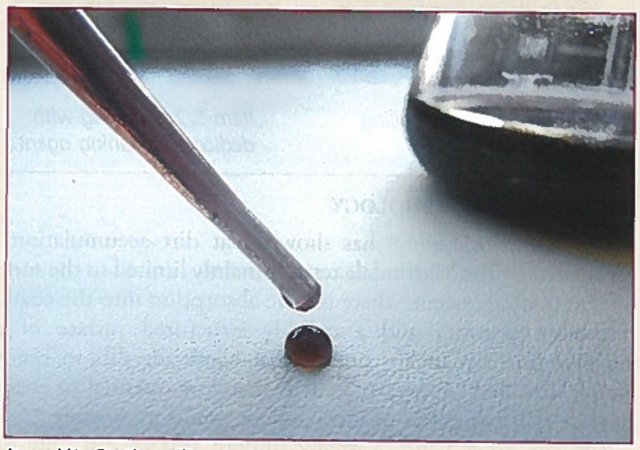
Testing the soiling behaviour of leather

There is a wide variety of tests to assess the soiling behaviour of leather. Static tests such as the 'coffee stain test' aim at simulating the accidental soiling of leather, with other examples such as spilled ketchup and mayonnaise as illustrated in *Panel 1, Item 1/1*.

Dynamic tests are more widely used. This is because they simulate the change of surface colour imparted by the constant exposure of the leather to dirt and different dyed fabrics.

These tests are usually carried out on Martindale test equipment, as shown in *Panel 1, Item 1/2*, according to the International Standard ISO 26082-1[Legend 1] using standardised 'dirty fabrics' as soiling probes[Legend 2] However, even though standardised equipment and materials are used, there are significant differences between manufacturers' requirements. This might relate to the number of cycles to be performed, the conditioning of the leather before and after testing, the operational mode of the equipment, and any cleaning operations to be performed.

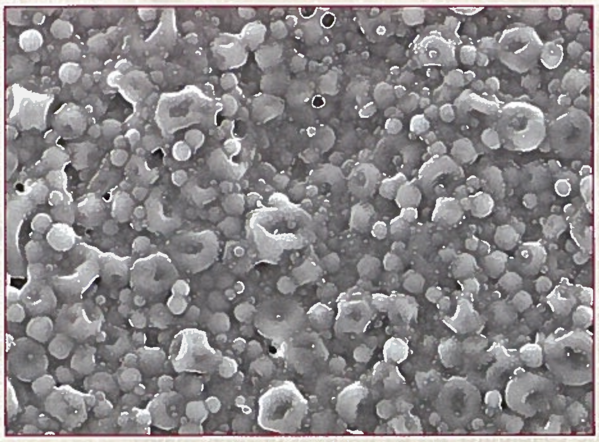
Panel 1: Static and dynamic soiling tests



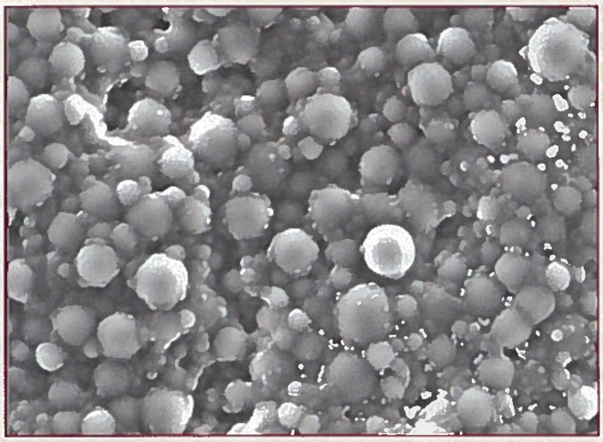
Item 1/1: Static soiling test.

Item 1/2: Dynamic test, with Martindale equipment.

Panel 2: SEM micrographs of standard and anti-soiling coating systems



Item 2/1: Standard coating.



Item 2/2: Anti-soiling coating.

The approach to anti-soiling systems

Three major factors need combining to develop a versatile anti-soiling system.

CHEMICAL MODIFICATION OF THE FINISH

Chemical modifications imparting a strong hydrophobic and possible oleophobic effect seem to be the obvious solution to improving the soiling behaviour of leather. This can be achieved by using additives such as silicones or fluorocarbons, or by incorporating fluorocarbon moieties into the base polymer of the coating.

Simple additions of silicone or fluorocarbon additives to conventional top coat systems show that, although these auxiliaries clearly imparted hydrophobicity - and in the case of fluorocarbons also oleophobicity - to the surface, no significant improvement in dynamic soiling behaviour could be obtained. In addition, a large amount of these auxiliaries has a significant undesired effect on the touch and feel of the surface.

Another drawback to the use of fluorocarbon auxiliaries is that they drastically reduce the adhesion of any corrective coating and therefore make a final colour adjustment impossible. The same is true for the use of fluorinated polymers in the coating. Silicones also reduce adhesion, but the effect is much less pronounced than with fluorocarbons.

However, only when combined with a coating system providing a suitable surface morphology do additives have a beneficial effect on dynamic soiling properties.

Panel 3: Soiling test results with EMPA 170-7-1172 (1000 cycles, 12 KPa, pilling mode)

Item 3/1: Standard coating. *Item 3/2: New anti-soiling coating.*

Panel 4: Soiling test results with EMPA 104 (300 cycles, 12 KPa, abrasion mode)

Item 4/1: Standard coating. *Item 4/2: New anti-soiling coating.*

Panel 5: Dye ingress test (1000 cycles, 12 KPa, abrasion mode)

Item 5/1: New anti-soiling coating. *Item 5/2: Cleaning with dedicated cleaning agent.*

THE SURFACE MORPHOLOGY

Previous work[Legend 3] has shown that dirt accumulation, as simulated by the Martindale tests, is mainly limited to the surface of the coating system: there is little absorption into the coating. However, porosity and a roughly structured surface of the coating provide 'anchor points' that allow the dirt to become firmly attached to the article. It is therefore essential to create a surface that has as few of these anchor points as possible.

On the other hand, a totally smooth surface can only be a glossy one, so a surface needs to be structured to a certain extent to appear matt.

The surface of a standard coating system based on an organic dull polymer is shown in *Panel 2* as *Item 2/1*. This sample was taken from a clean spot of an otherwise heavily soiled automotive seat, indicating that this type of surface is indeed prone to strong soiling.

In comparison the surface of a new anti-soiling coating system is shown as *Item 2/2*. Instead of the 'doughnut' shaped particles of the standard system, the particles of the anti-soiling system are spherical. This leads to a reduced number of holes and voids in the coat and therefore fewer anchor points for the dirt to attach to.

Optimisation of anti-soiling systems has shown that besides the shape and size of the particles effective crosslinking will improve the continuity of the film and reduce micro-porosity. This is another factor that has a strong influence of the soiling behaviour.

On the basis of these findings, a new anti-soiling system based on a matt water-based polyurethane dispersion has been developed.[1] Together with other auxiliaries, it provides a significantly improved soiling behaviour compared to other systems based on organic or silica-based matting agents. This is illustrated in *Panel 3* and *Panel 4* which show soiling tests that compare a standard coating system based on an organic dulling agent with the new anti-soiling system. Regardless of the test method used, the extent of the improvement is always immediately visible.

THE CLEANING COMPONENT

Leathers finished with this new anti-soiling coating system will stay clean over a much longer time span than conventional leathers, but over time, or under very harsh conditions, it is inevitable that some dirt will accumulate. The surface morphology of this new system, however, not only effectively reduces soiling, but it also makes cleaning soiled leather more easier and effective.

In this context it is extremely important to use a cleaning agent that does not cause damage to the coating and reduce the anti-soiling effect. For this reason a dedicated cleaning agent has been developed that removes dirt very effectively but leaves the surface structure intact[2].

The results of the so-called "dye ingress" test are shown in *Panel 5*. In this tough test a blue denim fabric is soaked in perspiration solution and then used in the Martindale test. The image shown as *Item 5/1* shows the excellent result obtained with the new anti-soiling system.

This leather was then cleaned with the dedicated cleaning agent. The result is shown as *Item 5/2* which shows that the dye can be removed completely.

Panel 6: Martindale soiling test results of anti-soiling versus standard top coat

Test Method	Standard topcoat	Anti-soiling topcoat	Requirement
Volkswagen PV 3968 EMPA 170-7-1172: 1000 cycles, pilling mode	2/3	4/5	> = 4
Jaguar/Land Rover TPLJR.52.211 EMPA 104: 300 cycles, abrasion mode	2/3	4	> = 4
Ford BN 112-11 Dye Ingress 1000 cycles, after cleaning	3/4	4/5	> = 4/5

The new anti-soiling coating system together with the dedicated cleaning agent will fulfil a wide range of manufacturers' requirements. *Panel 6* shows how leathers treated with this system comply with the original equipment manufacturers requirements compared to standard leathers.

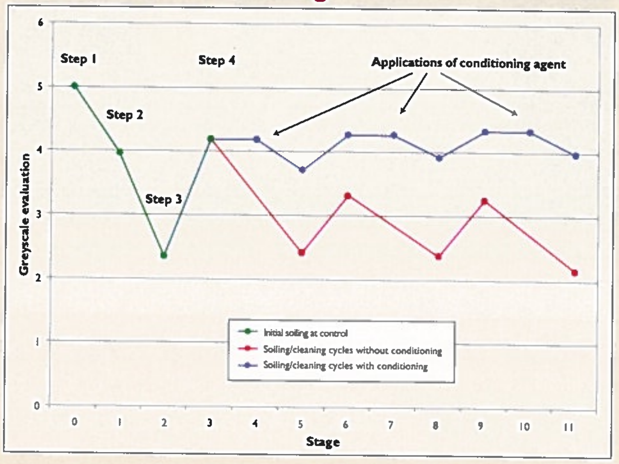
Extra conditioning for improved persistence of anti-soiling effect

An upholstery or automotive leather article is expected to have a long lifespan. During this time it is exposed to hard wear and may experience numerous cleaning cycles. Even the toughest coating system will undergo some changes of surface structure under these conditions, and this may lead to a deterioration of its soiling properties.

It has now been found that anti-soiling properties can be maintained and articles can be kept 'as new' by the application of a specially developed conditioning agent[3]. This conditioning agent can be applied as the very last step of leather production, as it will not alter the final shade or matting properties. It can also be re-applied by hand with a pad or sponge after cleaning and is therefore suitable as an after-treatment auxiliary for the final consumer or for servicing companies.

The effectiveness of this conditioning agent can be evaluated by subjecting a control finished leather to a series of soiling/cleaning cycles with and without the benefit of this agent and the findings are illustrated in *Panel 7*.

Panel 7: Persistence of anti-soiling effect with and without conditioning



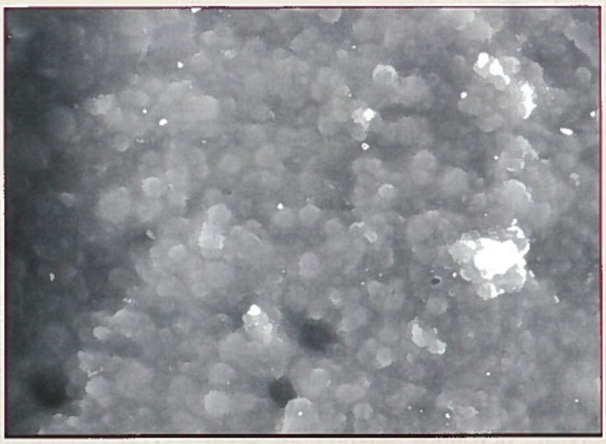
With reference to *Panel 7*, the following steps were followed:

Step 1: Leather was finished with the anti-soiling coating system as control, producing a Grey-scale evaluation of Grade 5.

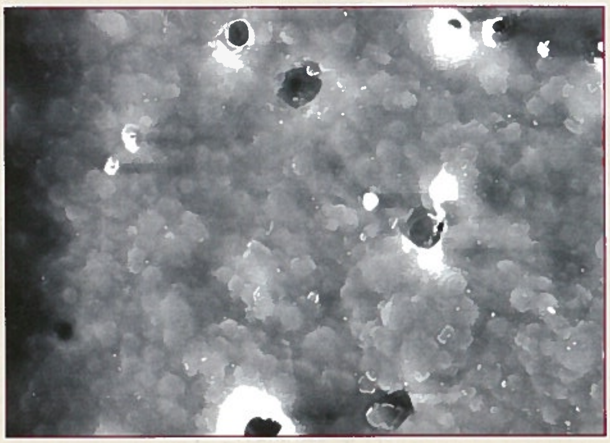
Step 2: This control leather was then subjected to a soiling test according to PV3968-1, producing a Grey-scale evaluation of Grade 4.

Step 3: The leather from Step 2 was then submitted to 200 cycles with the EMPA 128 dirt cloth. These combined soiling exposures represent a very tough test and are not normally applied together. At this stage soiling is clearly visible and Grey-scale evaluation drops to Grade 2 to Grade 3. (5 being the best and 1 the worst evaluation).

Panel 8: Soiling and cleaning cycles (no application of conditioning agent)

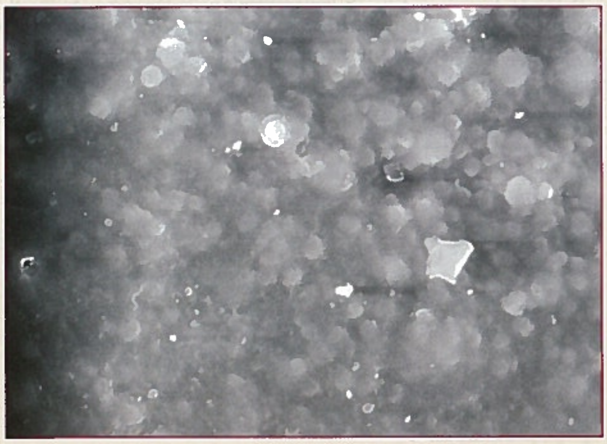


Item 8/1: Anti-soiling coating before soiling/cleaning cycles.



Item 8/2: Anti-soiling coating after soiling/cleaning cycles.

Panel 9: Anti-soiling coating after soiling/cleaning cycles and treatment with conditioning agent



Item 8/2: Anti-soiling coating after soiling/cleaning cycles.

Step 4: The leather from Step 3 was then cleaned. Most of this accumulated dirt was removed and the Grey-scale evaluation improved to Grade 4.

But after a second soiling *(as Step 2)*, and cleaning *(as Step 4)* a significant amount of dirt remains deposited on the surface and cannot be removed. The Grey-scale evaluation again drops to Grade 2 to Grade 3. More cycles of soiling and cleaning lead to a further decrease in performance as indicated by the red line shown in the graph.

However, when the leather was treated with the conditioning agent after each cycle of soiling and cleaning *(starting at Step 4)*, then the anti-soiling properties of the leather are fully maintained. This is indicated by the blue line shown in the graph.

The effect of the conditioning agent can be understood with the help of the SEM images presented in *Panel 8*:

Item 8/1 shows the surface of the reference sample finished with the anti-soiling coating, and *Item 8/2* shows the same sample after alternate soiling and cleaning operations. Some defects in the coating are clearly visible in these SEM images, but *Panel 9* shows

Panel 10: Stick-slip results of standard and anti-soiling coatings

24h standard climate + 3h / 23°C / 50% RH	**Max. RPN * (max. acceleration at 2 mm/s) F=10N**	**F=40N**
Standard top coat on smooth grain	5	5
Standard top coat on smooth grain	5	5
Anti-soiling system on smooth grain	2	2
Anti-soiling system on embossed grain	2	2
24h standard climate + 3h / 40°C / 90% RH	**Max. RPN * (max. acceleration at 2 mm/s) F=10N**	**F=40N**
Standard top coat on smooth grain	5	7
Standard top coat on embossed grain	5	5
Anti-soiling system on smooth grain	2	3
Anti-soiling system on smooth grain	2	3

** RPN=Risk-priority-number: 1 to 3: pass 4 to 5: tolerated 6 to 10: fail*