

USE OF NOVEL TETRAFLUOROETHENE COPOLYMER DISPERSIONS AS PROTECTIVE FINISH FOR LEATHER

by

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ABSTRACT

Antisoiling finishing is currently one of the most challenging topics in leather technology. Light colored leather articles are in vogue for high end applications like automotive and furniture upholstery. The leather surface should resist any type of matter that soils while maintaining all physical and aesthetical properties. Resulting from a joint development project between DAIKIN and LANXESS, a new aqueous polymer technology for leather finishing based on tetrafluoroethene (TFE) copolymers is being introduced by LANXESS.

In practice, formulations containing a TFE copolymer dispersion as the gloss binder, a specially designed matting agent and the appropriate additives are activated by a polyisocyanate and then applied on the leather surface using conventional spraying technology. A dual cross linking concept has also been developed for this new technology: Due to a chemical reaction, a fluorinated polyurethane network is generated on the leather surface thereby providing a permanently fixed protective coat and long lasting antisoiling effects. Compared to conventional systems, the resistance to any matter that soils is remarkably improved, whereas all physical properties remain unaffected.

RESUMEN

El acabado anti-mancha es actualmente uno de los temas más desafiantes de la tecnología de cuero. Artículos de cuero en colores claros están de moda para aplicaciones de alta gama como en la tapicería automotor y de muebles. La superficie de cuero debe resistir cualquier tipo de materia que manche mientras mantiene todas sus características físicas y estéticas.

Resultante de un proyecto común de desarrollo entre DAIKIN y LANXESS, una nueva tecnología de

polímeros acuosos para el acabado de cueros basada en copolímeros de Tetra Fluor Etileno (TFE) está siendo introducida por LANXESS.

En la práctica, las formulaciones contienen una dispersión de copolímero de TFE como capa de brillo, un agente mateante especialmente diseñado y aditivos apropiados que son activados por un polyisocianato y después aplicados en la superficie de cuero usando un soplete de tecnología convencional. Un concepto de reticulación dual también se ha desarrollado para esta nueva tecnología: debido a una reacción química, una red de poliuretano fluorado se genera en la superficie de cuero de tal modo que proporciona una capa protectora permanentemente fija y efectos anti manchas duraderos. Comparado a los sistemas convencionales, la resistencia a cualquier materia que manche se mejora notablemente, mientras que todas las propiedades físicas no son afectadas.

INTRODUCTION

Technical background

For some years, a significant trend towards light colored leather such as beige, pastel shades and even white leather, has been observed especially in car interior and upholstery leather. A major disadvantage of such light colored materials is that their attractive appearance is susceptible to soiling due to many factors. Car seats can become soiled due to color transfer from garments, air pollution, oil, fuel, and dyestuffs from food and beverages (e.g. coffee, tea, chocolate, spices and sauces). Additionally, accidental marks from cosmetics, pens, pencils, solvent based black permanent felt-pens or fluorescent text markers can also easily occur. These common stationery products are available in a wide range of colors and types and, once in contact with the leather, may quickly lead to a deterioration of the surface appearance. Furthermore, abrasion from everyday wear together with the heating of the car interior on exposure to intense sunlight and in combination with humidity, can irreversibly damage the leather's surface.

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With “high end” applications, such as automotive leather, the surface of the substrate can only be protected by applying a high performance finish. It is currently common practice to apply polyacrylic and / or polyurethane dispersions¹ that have been specially designed for this purpose to meet customers' requirements.

The special requirements for light colored leather articles can be summarized as follows:

- o Antisoiling properties: protection of the leather surface against irreversible contamination or damage by dirt and /or wear
- o Easy-to-clean properties: easy cleansing and efficient removal of any kind of dirt
- o Easy-care: long lasting protection of the surface after cleaning.

Additionally, the following normal specific characteristics of a high grade leather substrate to meet customers' expectations must be maintained:

- o Optical properties: e.g. grain pattern, visual color aspect and dullness
- o Acoustic effects on contact with other surfaces: optimized stick-slip behaviour to provide an antisqueak leather surface
- o Other sensory properties: e.g. touch, softness and surface smoothness
- o Thermal properties: heat stability of the finished leather and resistance against U.V. radiation
- o Mechanical properties: abrasion and fastness properties (e.g. cold and dry flexes).
- o Chemical stability: resistance against hydrolysis and common chemicals such as surface-active ingredients of cleaners; fuel, oils, lubricants, solvents, products used for personal care etc).

It is obvious, therefore, that a strong demand exists in the leather market for products that will meet the above mentioned criteria.

Concept

In order to improve the surface properties of leather, through chemistry, our target product design had to take into consideration the following key features:

- o conventional application techniques used for leather finishing
- o compatibility with other finishing products
- o aqueous based system (without organic solvents)
- o water and oil resistance
- o film forming properties
- o permanent fixation on the leather surface.

How to achieve this target? Our approach was to develop a special fluorinated polymer. Fluoropolymers have a unique position in application: they can provide oil repellency in combination with hydrophobic effects, chemical resistance and an extremely low surface energy. A high surface concentration of fluorinated molecules located on a leather surface, as a very thin coating layer, should be “dirt repellent”. As already mentioned above, in the case of leather many other properties have to be considered for the design of the chemical. For the leather finishing process, a solvent-free, aqueous product is required.

Most importantly, the resulting outermost surface of the leather substrate must be extremely hydrophobic. In contrast to this requirement, an efficient stabilization of polymer dispersions is only feasible by means of a special amount of hydrophilic groups at the polymer particle surface. However, these two effects, extremely hydrophobic behaviour of the final polymer in the coating and hydrophilic properties sufficient to make the polymer water dispersible, are clearly contradictory. This contradiction is resolved by a new synthetic concept for aqueous fluoropolymer dispersions.

For the polymer chemist the question is: How to introduce functional groups into the fluoropolymer to provide high crosslink density, sufficient hydrophobicity and antisoiling power as well? It must be emphasized that a product which does not have such functional groups will not achieve a permanent fixation on the surface. The polymer film formed will only be fixed permanently when there is an efficient cross linking due to suitable functional groups. Otherwise, the polymer film will dissolve on contact with solvents or may be wiped off even by rubbing with a soft pad containing an all-purpose cleaner. Beside these main prerequisites for polymer development, the target product additionally had to be especially designed to achieve optimal film forming properties such as Shore A hardness, elasticity, gloss etc., to make it function like a “normal” topcoat.

In this paper, we describe a new technology that meets all requirements mentioned above and even has additional advantages which will be covered below. Based on these results, a unique, new antisoiling system, consisting of a fluorinated gloss binder based on a new fluorinated copolymer dispersion¹ and a special matting agent² developed for this purpose as essential components, is now being introduced into the market.

CHEMICAL APPROACH

Chemicals for protection of leather surfaces against soiling and providing easy-to-clean properties are well-known. Many products have been proposed for this purpose but there is still a demand for improvement. For instance, dispersions of copolymers composed of perfluoroalkylethyl acrylate and methacrylate monomer units were introduced into the market many years ago. Typical polymers of this acrylic class are linear and have a comb-like structure wherein perfluoroalkylethyl substituents are fixed at the polymer backbone via ester linkages.

Very recent product development of coatings for rigid substrates demonstrates that it is even possible to obtain antigraffiti coatings² without use of fluorinated polymers. The final coatings are based on a highly crosslinked polymer network which provided a high gloss and a very smooth and tightly closed surface. For leather finishing, however, such polyfunctional polymers are too brittle and cannot be recommended because of poor flex resistance. Oil repellent surfaces are only available with fluorinated polymers. On the other hand, polytetrafluoroethylene (PTFE) and corresponding TFE copolymers³⁻⁶ are prominent examples of the extraordinary

General structure of the TFE copolymer

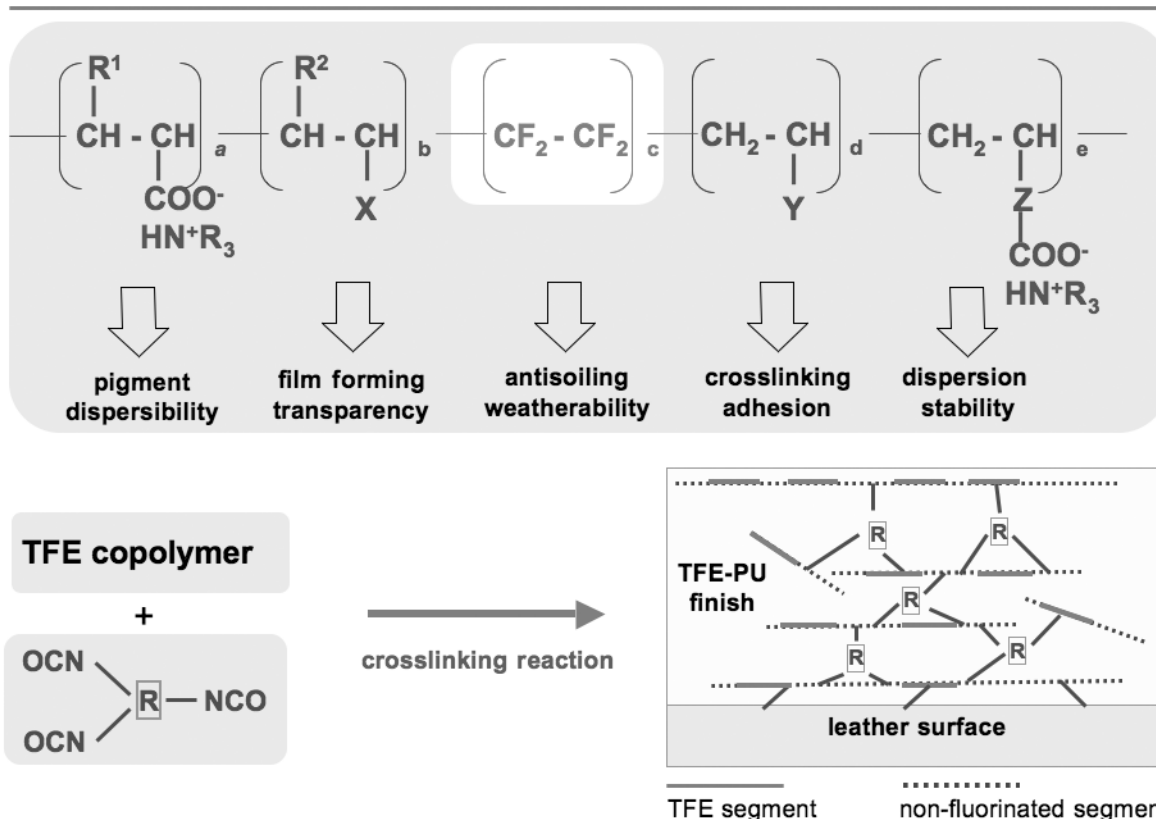


Figure 1: Structure of the new TFE copolymer used as the gloss binder. The new fluorinated polymer is composed of tetrafluoroethene (TFE) monomer units as the predominant building block. Even a total hydrolysis of this copolymer will not release low molecular weight fluorinated substances. The TFE units are fixed in the copolymer backbone by hydrolytically stable carbon-carbon bonds and would not be released even under strongest conditions of hydrolysis. The functional groups and other substituents introduced by copolymerization are located at the side chains of the copolymer.

After applying an aqueous formulation containing this TFE-copolymer and polyisocyanates as the crosslinker to leather a crosslinked coating is formed (below, right side).

high value they may add to consumer products. Heat resistant release coatings on pans or baking paper provide a high benefit. Technical application examples are low friction devices, fluoroelastomers for vehicles or machine parts. Furthermore, paints containing PTFE powder or other TFE copolymers are well established now and are advantageously used for anti-fouling coatings. Numerous applications have been found in the field of building conservation and in construction.

In the leather field, the incorporation of PTFE powders that are available in a broad range of particle sizes have failed to provide the required antisoiling effect. For instance, the mechanical performance of the topcoat is often affected because these particles are only embedded physically and may be chipped off during wear or result in a grey surface.

We herein present a new aqueous fluoropolymer finishing and coating system.

In close collaboration of R&D teams at DAIKIN and LANXESS, a new technology has been developed providing solvent-free aqueous fluorinated polymer dispersions that combine the unique antisoiling properties of TFE copolymers and the performance of established high performance topcoat systems for car seat applications.

CHEMICAL DESIGN OF THE FLUOROPOLYMER

The composition of the basic fluoropolymer has been optimized in our laboratories to meet the requirements for leather application. The final characteristics are shown below:

- o tetrafluoroethene monomer units were incorporated in the polymer backbone, thus generating exceptional oleophobic domains along the copolymer chain
- o monomers containing hydroxyl groups were introduced to achieve a high crosslink density in the resulting polyurethane surface film
- o monomers containing carboxylic groups provide stability of the product in aqueous dispersion
- o other comonomers were selected to adjust film forming properties and mechanical performance such as flexibility of the crosslinked film
- o hydrophobic monomers were used which enhance the hydrophobicity of the resulting coating

A schematic drawing of the structural features of the resulting optimized copolymer and their functions are illustrated in figure 1. In the presence of polyisocyanates³, the polymer forms a network that is chemically bonded to the conventional topcoat. Thus, a protective finishing layer consisting of a polytetrafluoroethene

^{19}F -NMR spectrum of the TFE copolymer

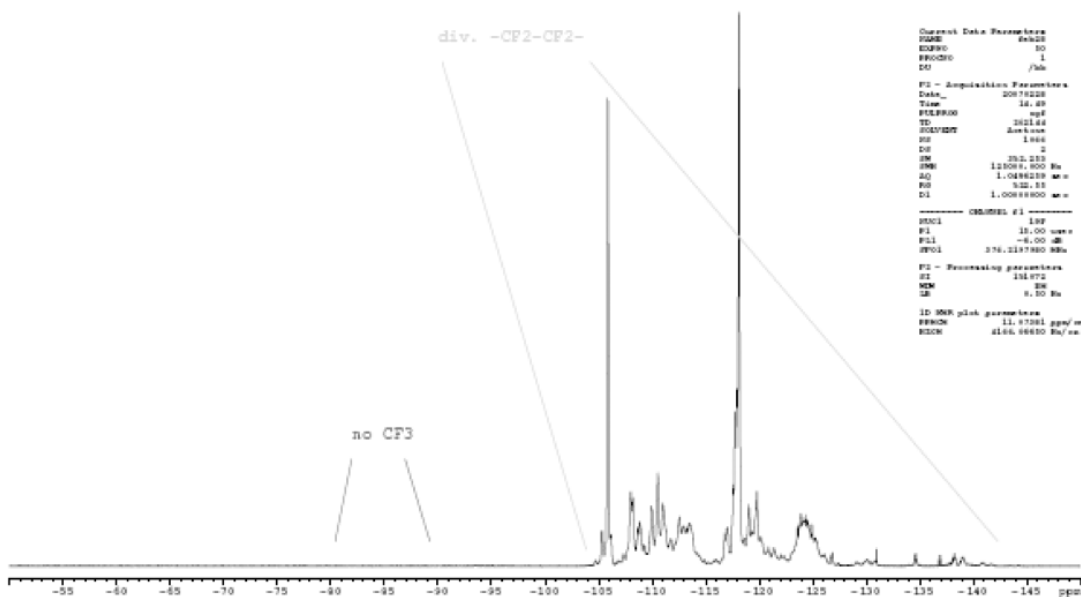


Figure 2: ^{19}F -NMR spectrum of the copolymer shown in figure 1. The spectrum shows different types of $-\text{CF}_2-\text{CF}_2-$ units of the PTFE segments. Remark: Resonances that may be attributed to CF_3 groups of perfluoroalkyl side chains or end groups of perfluorinated tensides (e.g. PFOS / PFOA or chemicals that may deliberate such unwanted substances) are not detected.

copolymer polyurethane network, a so-called PTFE-PU protection shield, is generated by the chemical reaction on the substrate.

According to the different copolymerization parameters of the comonomers used for the copolymerization process, a block-copolymer structure appears highly probable.

From ^{19}F -NMR spectroscopic investigation (figure 2) it is evident that the new copolymer has a segmented structure consisting of long-chain PTFE domains and shorter segments built up by other comonomers. From the ^{19}F -NMR spectrum, the absence of any CF_3 group is clearly proven.

SURFACE CHARACTERIZATION OF CROSSLINKED COATINGS BY DIFFERENT METHODS AND CORRELATION TO ANTISOILING PROPERTIES

Secondary ion mass spectrometry (SIMS)

In addition, the surface characterization of crosslinked coatings obtained with the gloss binder (according to figure 1) by ToF-SIMS clearly indicates that the fluorine distribution at the surface is homogeneous. This gives rise to uniform repellent properties.

Information about the uppermost surface layer of the coating was obtained with a lateral resolution of approx. 5 micrometers. Examination of the crosslinked film obtained by application of the fluoropolymer dispersion and a water-dispersible polyisocyanate on an aluminium substrate (figure 3) shows that the surface layer of the coating (evaluated surface area of extension 500 x 500 micrometers) has a uniform fluorine distribution when

considering the lateral distribution of elements. This is supported by the fact that the color intensity of the micrograph is homogenous.

X-ray photoelectron spectroscopy (XPS)

Additional analyses of the elemental composition of the surface using ESCA (XPS) (data shown in figure 4) demonstrate that the fluorine content is significantly reduced when going down from the outermost exposed surface layer in direction of the bulk volume. The bulk sample was analyzed after scraping off some material by means of a scalpel thus generating a new surface for characterization.

The experimental values for fluorine e.g. correlate with values calculated from the chemical composition of the coating. Vice versa, the nitrogen content at the surface is lower than at the bulk volume. Neglecting adsorbed traces of nitrogen from air the only nitrogen source is the crosslinker.

The increase of fluorine at the surface provides convincing experimental evidence which supports a model wherein highly fluorinated domains of the copolymer backbone (for example, loops of PTFE segments) are oriented towards the surface. Therefore, other elements are reduced accordingly. This can be visualized by the model picture shown in figure 5.

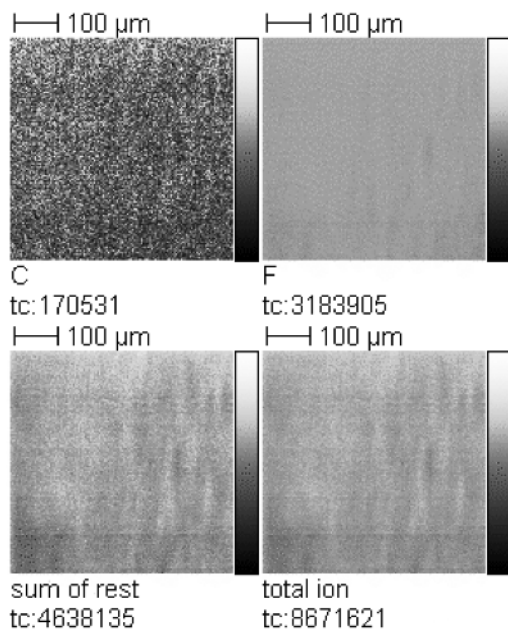
Surface characterization of leather samples by SEM

Leather samples finished with the new two component protection system that had been applied on top of a conventional automotive topcoat were examined by means of Scanning Electron Microscopy (SEM). An example is shown in figure 6.

Surface Characterization by ToF-SIMS

Substrate: aluminium plate coated with AQUADERM® X-Shield G + AQUADERM® XL 50 (polyisocyanate)

Field of view: 500.0 x 500.0 µm² F-Copolymer, Oberfläche M021512.MIF



Summary of surface analyses

- **homogenous lateral distribution of fluorine at the surface (SIMS)**
- **increased fluorine concentration at the surface (ESCA)**
- **no sulphur (ESCA, EDX) → no PFOS**
- **very smooth surface (SEM)**

Figure 3: SIMS micrograph taken from a isocyanate crosslinked fluoropolymer coating on an aluminium substrate (thickness 50 micrometers) showing the surface distribution of carbon, fluorine, sum of other elements except C and F and the total ion image at the uppermost surface.

Figure 6 shows a smooth surface without defects. The surface is dominated by the PTFE domains of the copolymer. The particles of the matting agent are responsible for the surface microstructure.

RESULTS AND DISCUSSION

A new system for leather protection has been developed having exceptional This novel AQUADERM® X-Shield system consists of 2 basic components, AQUADERM® X-Shield G (gloss binder) and AQUADERM® X-Shield M (matting component). The said system has been developed for the long lasting antistain/ antisoil finishing of leather. In addition, cleaning of a leather surface finished with these products will be very easy.

The antisoiling performance has been proven by using artificial dirt and a broad range of real food, beverages, cosmetics and office-markers etc. Different cleaners were also tested and the tests were run by hand and under best reproducible test conditions that are accepted by the automotive industry e.g. the Dye Ingress Test and also according to the new drafted VDA test etc. The leather finishing system has been optimized to meet the highest requirements of the automotive leather industry. Following the recommendations of LANXESS' leather technicians, leathers can be produced that will pass all available antisoiling tests and even more.

General aspects for application

The first essential component of the new protection system is an aqueous dispersion of a crosslinkable TFE copolymer with film forming properties. Dried films are clear, flexible and characterized by a high gloss surface and a hardness of 50-60 Shore A (without crosslinker).

The combination of this component with a polyisocyanate crosslinker results in a leather coating that shows outstanding cleanability and also excellent mechanical resistance and fastness properties. The coating provides high gloss, a dry touch and a perfect, smooth surface having excellent weatherability on U.V. exposure.

In general, automotive leather has a relatively dull surface to avoid or reduce reflections of incident light. The degree of dullness is adjustable by the second component of the new system, a special matting agent that has been designed for application in combination with the gloss binder. This matting agent is an essential component in order to get the desired dullness without impacting the antisoiling properties.

The duller has also film forming properties and is crosslinkable due to the special binder mixture. It has been proven that the degree of surface dullness is easily adjustable to the customer's requirements simply by the correct selection of the ratio between gloss binder and matting component.

Surface characterization by ESCA (XPS)

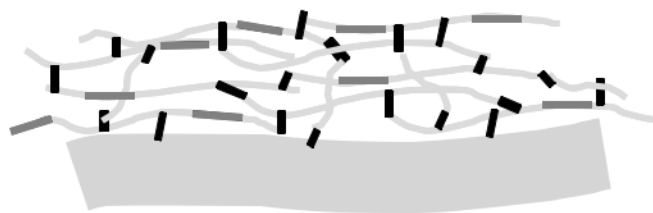
No.	ESCA–quantification [atom%]	F	O	N	C
1	fluoropolymer surface* (60° angle), ca. 6 nm information depth	21.3	6.5	17.9	54.3
2	fluoropolymer surface* (0° angle), ca. 10 nm information depth	20.5	6.9	21.4	51.2
3	fluoropolymer* (after scratching with scalpel), bulk volume	16.1	7.6	27.6	48.7
	calculated values	21.5	5.1	13.6	50.3

* Substrate: aluminium plate coated with AQUADERM® X-Shield G + AQUADERM® XL 50 (polyisocyanate);

ESCA: large area measurement = 5 mm², max. information depth ca. 10 nm

Figure 4: Data of XPS spectra obtained for a surface prepared in the same manner as for figure 3. The elemental composition of a crosslinked high gloss coating is indicated. Concentrations of fluorine, oxygen, nitrogen and carbon at different depth of the coating layer are given in atom %).

Model of the segmented TFE-PU coating layer



polyisocyanate crosslinking



X-Shield polymer with TFE segments

Figure 5: Model of a cross linked coating (so-called PTFE-PU coating layer) on leather.

Loops of longer PTFE segments located at the surface are visualized as separate bars.

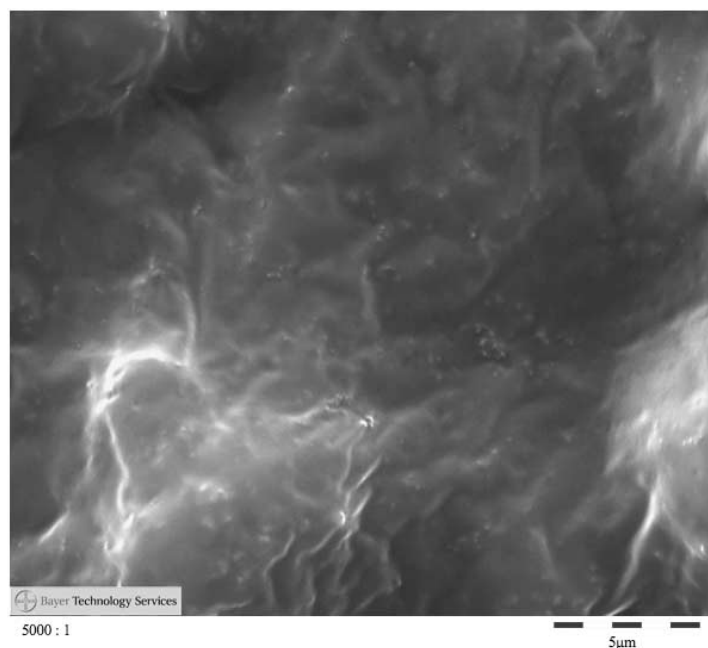


Figure 6: SEM micrograph of the surface of a finished leather sample after application of a formulation containing the fluorinated gloss binder, matting agent, additives and crosslinker on a conventional automotive topcoat. Length of scale bar: 5 micrometers. (method: topography contrast), magnification: 5000:1 (ID: E015003RE104, 28-02-2007)

The most appropriate crosslinkers to be used in combination with this new system are water dispersible polyisocyanates³. Recommended also, but not absolutely necessary, are carbodiimide type crosslinkers that can be used in combination with polyisocyanates. Other crosslinkers that are widely used in the leather industry may be applied, but the best performance is obtained with polyisocyanates.

The amount of crosslinker used is one of the most important parameters to consider in order to achieve the maximum performance. Performance also depends on the final ratio of gloss binder and matting component. As a rule, the

polyisocyanate is used in an excess of about 50% compared to NCO-reactive groups being present in the polymer.

Guidelines for leather application

The new protection finishing system is applied as the sole topcoat using conventional spray finishing techniques.

For permanent antisoiling effects crosslinking is necessary. After application of the system on the substrate and subsequent drying a crosslinked film, chemically fixed to underlying "normal" leather finishing layers, is formed. The already excellent performance of the polyisocyanate crosslinked antisoiling topcoat can be further improved by a dual crosslinking mechanism when using polyisocyanates in combination with a polyarabodiiimide⁴.

Typical formulations of the new antisoiling system contain pigments, flow and touch modifiers as well as crosslinkers and are applied as the final layer. Provided the correct additives⁸ have been selected, the resulting finish also exhibits a pleasant feel and an antisqueak performance.

The formulations can be applied onto leather using all state-of-the-art application technique and meet, once completely crosslinked, the most extreme requirements with respect to antisoiling performance, cleanability and physical fastness properties.

It is recommended to apply an amount of 1.5 - 2.0 g/ sq. ft. (formulation according to figure 7). Corrections are possible directly after application, although it is recommended to try to avoid it.

Antisoiling properties of leather

A conventionally finished automotive leather was used as the substrate for coating with the fluoropolymer system. For evaluation of the antisoiling performance and cleanability a screening test has been developed which allows for application of a broad range of contaminants or dirt. For this purpose, a test panel consisting of small leather pieces coated with a formulation according to figures 7 were cut out from the same material.

Product	Type	Parts
AQUADERM® X-Shield G	antisoiling binder component	140
AQUADERM® X-Shield M	antisoiling matting component	210
Pigmentmix	adjustment of shade	20
Water		460
ACRYSOL™ RM-825, RM-1020	thickener	5
AQUADERM® Fluid H	levelling agent	5
AQUADERM® Additive GF	touch modifier	40
AQUADERM® Additive SF	touch modifier	30
AQUADERM® XL50	crosslinker 1	70
BAYDERM® Fix UCL	crosslinker 2	20
Sum		1000

Figure 7: Guideline for a typical formulation for antisoiling finishing of leather.

Cleanability test panel

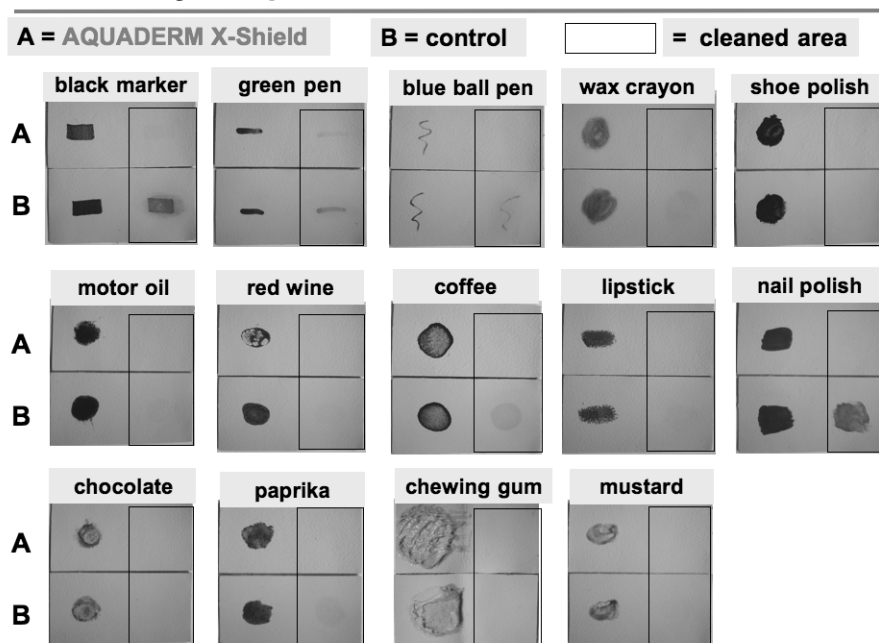


Figure 8: Laboratory test panel for evaluation of the antisoiling performance and cleanability of automotive leather finished with the fluoropolymer formulation shown in figure 7. Dirt: black permanent marker (xylene based), green felt pen, blue ball pen, wax crayon, shoe polish, motor oil, red wine, coffee, lipstick, nail polish, chocolate, paprika, chewing gum, mustard.

Cleaned by hand 1 day after application. Cleaned areas are marked by a rectangular frame. Each leather specimen with antisoiling finish (row A) is also compared with a control (row B) wherein the conventional automotive leather sample (without antisoiling finish) was treated in the same way.

The selected soiling matter was applied twice to each leather piece. The samples were then left for one day at ambient temperature. After drying, the cleanability was evaluated by rubbing with a soft pad wetted with a cleaner. (We attempted to remove one spot by cleaning and the other was kept as a reference). This was done by hand or with a Veslic tester under a given set of parameters. Then the residual dirt was evaluated by visual inspection in daylight. This method allows a very quick and simple evaluation.

A selection of different matter that soils, given in figure 8, demonstrates that the leather finished with the AQUADERM® X-Shield system is easily cleaned. The most problematic dirt, such as the black permanent marker, could be wiped off with only a few rubs with a soft pad and cleaner.

While a Martindale apparatus was also used, the type of dirt, load and number of cycles as well as computational conditions vary from case to case. For instance, the so-called Dye Ingress test is preferred by some European car manufacturers. In Asia, for example, another test method has been proposed, namely using permanent black marker that is very hard to remove from conventional surfaces, different colored office pens, mustard, lipstick, red wine etc.

Furthermore, a new standard procedure was proposed very recently by the VDA in Germany using the Martindale apparatus for application of dirt and a new type of dirt developed especially for this test method. After dividing the soiled area in smaller pieces and also exposing some of the specimen to U.V. light and/or hydrolysis, the cleanability is tested with the original

leather surface as the reference. This procedure has been proposed as a new standard method for the automotive industry, but is still under discussion.

As illustrated by the examples shown in figure 8, leather finished with a formulation containing the new TFE copolymer dispersion will pass all known test methods. Even after mechanical damage of the surface by scratches or abrasion due to normal wear, the remaining amount of PTFE segments at the leather surface is high enough to maintain the antisoiling properties.

Extended contact time of the dirt or staining components does not have a severe effect on the cleaning results. After treatment with cleaner, a very careful inspection of the leather surface indicates that there is no abrasion or any other damage of the surface. After repeated cycles of dirt application and subsequent cleaning, applied to identical surface areas, the same positive results are achieved.

Statement for PFOS and PFOA

In recent years, the discussion about fluorinated surfactants, especially perfluorooctane sulfonic acid and perfluorooctanoic acid, have been prominent in the media. These have been used as process auxiliaries during the manufacture of fluoropolymers and may also be released as the final product in a degradation sequence of polymers that contain such structural units in their side-chain. These discussions have led to the position that such substances should be avoided in the future. Regulations have indeed already been implemented that impose a control on certain applications and in some cases such substances are now banned from use⁹.

As already demonstrated by the NMR spectrum, the TFE copolymer dispersions described herein do not contain PFOS, PFOA or any other perfluorinated emulsifiers, because we did not use any raw material containing these by-products. Furthermore, this has been confirmed by BLC through analysis of a finished leather sample treated with the formulation according to the guidelines given in figure 7. It has been confirmed that the concentration of both substances is below the detection limit of the analytical method (< 10 micrograms / kg).

CONCLUSIONS

Results indicate that the specially designed aqueous finishing system based on a crosslinkable tetrafluoroethene copolymer dispersion and a special matting agent is able to make light colored leather surfaces resistant to all kinds of matter that soils. Furthermore, the leather surface can be easily cleaned with common cleaning agents.

It has been shown that the performance characteristics depend on the ratio between the crosslinker and gloss binder / matting component. The surface dullness can be easily controlled by adjusting the amount of a special matting agent that has also been developed for this antisoiling system. A typical formulation for leather finishing has been proposed in this article. The AQUADERM® X-Shield system is applied as a final topcoat onto state-of-the-art-finished leathers using conventional spraying technique. With this new system¹⁰ the most rigid standards of the automotive industry for testing fastness properties can be easily passed. Dual crosslinking by special crosslinker combinations can even further improve the antisoiling performance.

EXPERIMENTAL (SYNTHESIS) DETAILS

Materials and Methods

All reagents and chemicals used for synthesis were of analytic grade and used without further purification. Products used for formulation and application were commercial products. The fluorinated polymer precursor was provided by DAIKIN Industries as a solution in an organic solvent.

For characterization of products, standard analytical laboratory methods were used to determine solids content, pH, density, particle size distribution, purity etc. ¹⁹F-NMR-spectra were recorded in acetone by a NMR-Service Laboratory at BAYER Industry Services. Model substances for structural correlations were synthesized according to known methods.

Surface characterization by Scanning Electron Microscopy (SEM) including topographic analysis of leather by EDX as well as investigations of coatings by XPS (X-ray photoelectron spectroscopy, ESCA) and ToF-SIMS (time-of-flight secondary-ion mass spectrometry) were made by service laboratories at BAYER Technology Services.

Procedures

Synthesis of the aqueous TFE copolymer dispersion (gloss binder)
A tetrafluoroethene (TFE) copolymer characterized by an acid

value of 9 mg KOH/g, an OH-value of 60 mg KOH/g and a number average molecular weight of approx. 20000 g/mole was chemically modified by partial reaction of OH groups in an organic solvent. After complete conversion, the polymer was dispersed in water and the solvent was removed by distillation.

A milky-white aqueous dispersion is obtained characterized by a solids content of 40% by weight, viscosity < 30 mPas (20°C, 10 s⁻¹) and a pH-value of approx. 7.

Synthesis of the matting agent

A special mixture of binders containing a special fluorinated polymer, matting agent and well-selected auxiliaries were intimately mixed by means of high shear equipment e.g. dissolver or rotor stator system. The resulting white dispersion has a solids content of 30 % by weight and a viscosity of approx. 2000 mPas (20°C) for easy handling.

Preparation of the finishing formulation

The gloss binder and the matting agent described above were formulated with properly selected additives such as flow agent, levelling agent and pigment mixture for color adjustment. The viscosity was adjusted by addition of thickener and water. Finally the mixture was activated by addition of an appropriate type and amount of crosslinker.

thickener: e.g. commercially available non-ionic polyurethane⁵,
crosslinker 1: water-dispersible polyether-modified aliphatic polyisocyanate⁶,
crosslinker 2: water dispersible aliphatic polycarbodiimide⁷,
flow control agent: polyether-group containing, water-dispersible polydimethyl-siloxane⁸,
touch modifiers: special silicone-based products⁹.

Application of the formulation

Automotive crust leather was prepared according to known methods using wet blue as the raw material and a state-of-the-art process for retanning / dyeing / fatliquoring. The crust was finished using formulations with proven efficacy for high performance automotive leather.

Finally, the fluoropolymer finish formulation described above was applied on the topcoat of the leather sample by spraying. The amount of formulation depends on the desired effect, however 1.5 to 2.0 g wet / sqft are sufficient in general (approx. 0.4 g dry / sq. ft). After spraying the leather was dried under standard conditions in a drying chamber. It was then horsed up and left at room temperature.

Leather Evaluation

For physical testing, samples were cut out and conditioned at room temperature at 50% relative humidity for 24 hours before evaluation and surface characterization. Dirt and cleanability tests were run 2 days after spraying.

The leather performance regarding Bally flexes (dry, cold), rub fastness (Veslic wet, dry; Taber abrasion; Wyzenbeek etc.), U.V.

stability, hydrolysis and thermal stability etc. was evaluated according to standard methods.

The antisoiling behaviour and the cleanability of leather specimen were evaluated by different methods that are already introduced in the automotive industry. The main difference of these tests are the composition of dirt, type of cloth, the equipment used, the number of cycles, time used for application and the interval between application and cleaning.

For instance, the Dye Ingress test (demand of some European car manufacturers) uses a Martindale apparatus. Another test method - proposed by Asian facilities - uses e.g. permanent markers, ball pens and selected cosmetic articles and food ingredients as test substances. Furthermore, a third method uses drops of coffee, chocolate or motor oils that are applied directly on the surface until drying.

Additionally, the leather samples were also examined according to a new method very recently proposed by the VDA in Germany that is still under discussion for approval.

Laboratory screening cleanability test

A black oil ink pen and a black solvent based permanent marker were applied to the leather surface and left for a given time at ambient temperature. For removal of any traces originating from applied dirt, e.g. ballpoint pen, a mild detergent solution (commercial Leather cleaner) was applied to a cloth which was then used to wipe off as much as possible.

More resistant spots (e.g. permanent marker spots) were treated similarly, but in this case a piece of cloth to which a little amount of a commercial cream for leather care had been applied was rubbed over the marker trace to remove as much as possible. A second piece of cloth prepared with fresh cleaner was rubbed over the trace by circular movement and light pressure. The cleaning effect was evaluated visually against the untreated original.

This test is also very useful for application of other types of "dirt" such as cosmetics, food and beverages.

We used, for example, commercially available leather cleaners¹².

Martindale test

The Martindale apparatus is recommended by many producers of automotive leather as well as car manufacturers for the evaluation of antisoiling properties of leather.

Leather samples with a diameter of 150 mm are placed onto the fixed sample holder of the apparatus. In a special embodiment a piece of blue jeans cloth wetted with synthetic alkaline sweat solution was exactly positioned in the opposite holder representing the moving part of the machine. During the test cycles the wet jeans cloth is rubbed over the leather surface under constant load (applied to each movable holder, e.g. 50 N). The

circular movements are described by a Lissajous-pattern, causing a square shaped application of dirt. After 1000 cycles the leather samples were removed and evaluated for color changes. Then the leather samples can be re-positioned in the apparatus for testing the cleanability. In this case, a cotton cloth wetted with a detergent solution was rubbed against the leather surface. The final color difference was compared with the untreated sample.

Depending on the method, the cleanability may also be tested by hand as proposed by the drafted VDA norm.

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FOOTNOTES

1. AQUADERM X-Shield G (product from Lanxess)
2. AQUADERM X-Shield M (product from Lanxess)
3. E.g. products of the AQUADERM® range such as AQUADERM® XL 50, XL 70, XL 80, XL DI etc.(products from Lanxess)
4. e.g. BAYDERM® Fix UCL (product from Lanxess)
5. ACRYSOLTM RM-1020, 20% conc., or ACRYSOLTM RM-825, 25% conc. (products from Rohm and Haas),
6. AQUADERM® XL 50, 50 % conc.(product from Lanxess)
7. BAYDERM® Fix UCL, approx. 50% conc. (product from Lanxess)
8. AQUADERM® Fluid H, 100% conc. (product from Lanxess)
9. AQUADERM® Additive GF and AQUADERM® Additive SF (products from Lanxess)
10. E.g. the cleaning stick Ink Away™ (product from Leathermaster)

INTRODUCTION OF THE HEIDEMANN LECTURE

by
ELEANOR BROWN

Professor Eckhart Heidemann of the Darmstadt school was the leading collagen, as related to leather, scholar of the second half of the twentieth century. Prof. Heidemann's research was a blend of fundamental collagen studies with practical tannery applications. During his lifetime, Professor Heidemann instituted the practice of scheduling a biennial symposium, featuring leading collagen researchers of the world. These Heidemann symposia were held in the afternoon prior to the start of each IULTCS meeting, and developed a scientific basis for more practical talks to come.

In recent years, the symposium has evolved into a Heidemann memorial lecture to open the technical program of each IULTCS Congress. ALCA, as host of the 29th Congress, assigned the selection of the Heidemann speaker to its collagen committee. The committee recognized that a major challenge for leather scientists and technicians of the 21st century, who will be expected to develop chrome free leathers, is to understand at the molecular level the effects of tanning processes on collagen. The ability to visualize realistic collagen assemblies, not just triple helical peptides, under the environmental conditions of tanning is an important step in this direction.

The selection committee was unanimous, as was the ALCA Council on the selection of Dr. Lorenz Siggel as the 2007 Heidemann lecturer. Dr. Siggel earned a PH.D in 1986, in physical organic chemistry from Oregon State University. In 1988, following post-doctoral stints at the Max-Planck Institute for Medical Research in Heidelberg, Germany and Stanford University in Palo Alto, CA, he joined BASF AG in Ludwigshafen, Germany as a computational chemist. From 1988 to 2000 he modeled everything from homogeneous and heterogeneous catalysis to polymers, biodegradability of metal complexing agents and photochemical reaction mechanisms. After transferring to the life science modeling group in 2000 he concentrated on agro and specialty chemicals. Lorenz began modeling collagen as applied to leather in 2003 in collaboration with the polymer-modeling group at BASF. His topic today is "Leather related collagen modeling: The challenges of modeling hierarchical structures".

Please join me in welcoming Dr. Lorenz Siggel, the 2007 Heidemann Memorial lecturer.
