Hydrocarbon Surfactants as Wetting, Flow and Leveling Aids for Floor Polishes

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Recent discoveries regarding persistence, bioaccumulation and toxicity have led to increased scrutiny of many fluorosurfactants by global regulatory agencies. Fluorosurfactants have been the dominant additive as wetting, flow and leveling aids in floor polish formulations for many years. Because floor polishes are ultimately removed and disposed to wastewater streams, and municipal waste water treatment facilities are unable to process certain fluorosurfactants properly, perfluorinated acid degradation products might be introduced into the environment. The presence of perfluorinated acids in the environment has become a global concern. As a consequence, there is a desire to formulate floor polishes using hydrocarbon instead of fluorochemical surfactants.

Floor Polish Performance and Regulatory Climate

Flooring substrates comprise a variety of materials and forms. Floor polishes are true coatings formulated to seal, protect and enhance the appearance of substrates onto which they are applied. Floor polish technology is dominated by acrylic copolymers designed to have very specific utility; although, some innovations, such as a new class of styrene-butadiene (SB)-based copolymers recently introduced by OMNOVA Solutions Inc., have found commercial success. Changes to global legislation and environmental considerations require a constant review of formulating ingredients. This is true particularly to ensure compliance with a number of sponsored programs such as the United States Environmental Protection Agency's “Design for the Environment” and “Nordic Swan” in Europe.

A floor polish formulation must satisfy several basic criteria. The glass transition temperature, T_g, of a polish copolymer must be low enough to form a film at room temperature, yet high enough to impart mechanical properties such as black heel mark resistance and robustness to burnishing. The effective T_g of the copolymer is modified by addition of plasticizers and coalescents designed to optimize performance. Furthermore, wax emulsions are usually added to the floor polish formulation to aid in final film coefficient of friction, promote durability and further enhance the black heel mark resistance attributes.

Dried film mechanical properties ultimately are determined through non-covalent cross-linking interactions between an alkaline earth metal or other divalent metal salt and a functionality on a monomer used to make the copolymer (e.g., acrylic acid). This allows the floor polish to be removed using an alkali solution to eliminate cross-links and solubilize the copolymer. In addition to mechanical properties, a floor polish must provide good optical properties such as gloss and distinctness of image.

Ultimately, the floor polish composition must wet the substrate, which often is contaminated with a variety of low tension substances. The floor polish composition then must flow and level on the substrate.

Historically, fluorosurfactants have been the materials of choice as wetting, flow and leveling aids in floor polish coatings. The process of wetting has been defined mathematically in Young's equation [1]

$$\gamma_{lv} \cos\theta = \gamma_{sv} - \gamma_{sl}$$

where γ are interfacial tensions at the liquid-vapour (*lv*), solid-vapour (*sv*) and solid-liquid (*sl*) interfaces and θ is the contact angle between the wetting liquid and the substrate. According to Young's equation, a liquid must have a lower surface tension (γ_{lv}) than the substrate (γ_{sv}) to which it is applied in order to wet that substrate. Herein lies the dilemma. Pure water has a much higher surface tension (~ 73 mN/m) than most substrates of interest (floor tile in this case with $\gamma_{sv} \approx$ 30-40 mN/m). This is not a favorable condition for wetting and the liquid will have a relatively high contact angle on the substrate. The situation is exacerbated when floor tiles are contaminated with low surface tension materials, which further decreases the surface tension of the substrate.

Comparison of Fluorosurfactant and Hydrocarbon Surfactants

Fluorosurfactants typically have several advantages over hydrocarbon surfactants. [2] Fluorosurfactants efficiently reduce surface tensions of coatings or liquids into which they are added to values in the range of 18-28 mN/m. This surface tension value is lower than either the substrate or any possible nonfluorinated contaminant and ensures good wetting of the substrate. Fluorosurfactants are also quite effective in achieving minimum surface tensions (at the critical micelle concentration; cmc) in the concentration range of 50-500 ppm.

Some hydrocarbon surfactants are capable of reducing surface tensions to the ~ 25-30 mN/m range, albeit at much higher concentrations. Therefore, the most efficient hydrocarbon surfactants can indeed lower the surface tension of coating below that of either the substrate or contaminant and allow for proper wetting according to Young's equation.

Flow and leveling issues are far more complicated and still somewhat of a mystery in regards to floor polish performance. A typical floor polish formulation has many interfaces, components, surfactants and particles, and is a dynamic system due to drying, curing, cross-linking and/or vitrification.

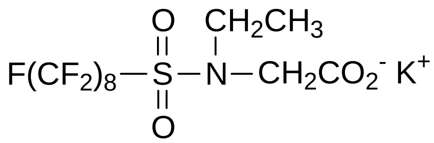
In the simplest case, the leveling stress, *s*, of a pure liquid is given by [3]

$$s = \frac{\gamma_{lv}}{r}$$

where *r* is the radius of curvature of the surface; more simply, $s \propto \gamma_{lv}$. Therefore, one would expect that *increasing* the surface tension of the liquid and not *lowering* it, would lead to flatter or more level films. This seems contrary to the use of surfactants that are designed to provide very low surface tensions such as fluorosurfactants.

The argument presented above points to the complexity of flow and leveling in multicomponent and dynamic coatings such as floor polishes. In reality, the complexity and dynamics of coatings are such that a variety of gradients are presented. Temporal and spatially-variant surface tension gradients can result in what is known as Marangoni flow. Marangoni flow leads to mass transport and defects such as "picture framing", "cratering" and "Bénard cells". [4-6] Operative mechanisms for flow and leveling afforded by fluorosurfactants (or low surface tension surfactants, in general) include reduction of gradients that induce mass transport.

Fluorosurfactants, however, are not without issue. Prior to 2001, 3M's Fluorad® FC-129 fluorosurfactant, shown below, was the archetypical C8-based surfactant and the fluorosurfactant of choice.



Surfactants from other suppliers are often based on telomers of tetrafluoroethylene where there is a distribution of perfluoroalkyl chain groups with an average perfluoroalkyl chain length ($F(CF_2)_n$, $n \approx 8$). In 2001, 3M decided to exit the C8-based surfactant market because of mounting data concerning persistence, bioaccumulation and toxicity. The greatest concern was not the surfactant as-supplied but, instead, a potential perfluorinated acid degradation product. [7-9]

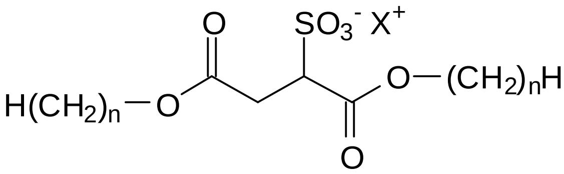
$$F(CF_2)_nCOOH$$

Persistence, bioaccumulation and toxicity of perfluorinated acids increase in a power law fashion with increasing perfluoroalkyl chain length. Currently, there is much global regulatory scrutiny of properties of fluorochemicals, fluorosurfactants and potential degradation products, and the industry is in flux. It would simplify the situation for many manufacturers if they were able to remove fluorosurfactants from formulations entirely.

In simplistic summary, for a surfactant to function as a wetting, flow and leveling agent in floor polish, or coatings in general, it must be the lowest tension component in the formulation and have a surface tension less than that of the substrates it is intended to wet.

Sulfosuccinate Hydrocarbon Surfactants As Viable Alternatives

A class of twin-tailed, sulfosuccinate hydrocarbon surfactants may fit the aforementioned criteria to function adequately as wetting, flow and leveling aids in floor polish formulations. A generic sulfosuccinate surfactant is illustrated below.



Sulfosuccinate amphiphiles fall into a general category know as "gemini" surfactants. [10-15] Due to this gemini or twin architecture, very low surface tensions, in the ~ 25-30 mN/m range, can be reached with surface tensions proportional inversely to hydrophobe chain lengths.

Experimental Using SB-Based Copolymer

Experimental data reveals properties obtained for several floor polishes formulated with and without a fluorosurfactant using a variety of commercially available surfactants including sulfosuccinate derivatives.

A model floor polish composition based on a new styrene-butadiene copolymer is given in Table 1. The new poly(styrene-butadiene)-based floor polish is marketed commercially as Omna-Glo™ 100 (OMNOVA Solutions Inc.). [16] All ingredients, except the last, are mixed for 10 minutes before the styrene-butadiene (SB) latex is added followed by an additional 30 minutes of mixing. For comparison, Zonyl® FSJ fluorosurfactant (DuPont) was tested also in the model formulation. The fluorosurfactant (and a small amount of water) was replaced with the hydrocarbon surfactants shown in Table 2 creating formulations shown in Table 3.

Formulations 3 (at 400, 600, 800, 970 and 1300 ppm) and 20, along with two comparative formulations employing Zonyl® FSJ fluorosurfactant (one of which was prepared using the formulation from Table 1, and the other made from a slightly different formulation) and a control employing no leveling aid, were applied to a test floor as part of a burnishing trial.

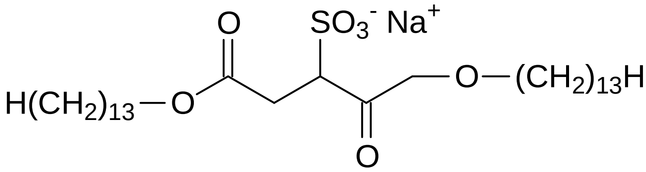
All of the compositions levelled well on the first coating application but, after the second application, formulation 20 showed application lines while the control formulation had a blotchy, “leopard skin" pattern; Formulation 3 (all amounts) and the fluorosurfactant-containing formulations showed good leveling performance. The coatings provided from the five versions of formulation 3 and from one of the fluorosurfactant compositions were evaluated for slip and gloss before being burnished in the following sequence:

(1) polishing pad (400 rpm),
(2) abrasive pad (400 rpm),
(3) polishing pad (400 rpm)
(4) polishing pad (1500 rpm).

After each burnishing, the slip and gloss of each coating were measured again. The slip performance of each coating was excellent or close to excellent at each point in the testing, while the gloss measurements are summarized in Table 4. Gloss was measured using a Sheen Tri-Glossmaster at 60° using ASTM-D-1455-87.

Results and Discussion

Wetting, flow and leveling of a styrene-butadiene copolymer-based floor polish formulation was tested with a variety of hydrocarbon and fluorocarbon surfactants including a telomer- and C2-based materials. Shown in Table 1 is a model styrene-butadiene copolymer-based floor polish formulation. The hydrocarbon and fluorocarbon surfactants tested are detailed in Table 2. It is important to differentiate the surfactants listed in Table 2. Zonyl® FSJ (not shown in Table 2) is the “benchmark”, telomer-based fluorosurfactant in floor polish formulations and PolyFox™ PF-154N is a C2-based fluorosurfactant. Edaplan® LA 451 is a bis(tridecyl) sulfosuccinate while Aerosol® OT-70 is a dioctyl sulfosuccinate. The structure of Edaplan® LA 451 (sodium bis(tridecyl) sulfosuccinate) is given below.



Each composition was applied in two coats to vinyl tiles. Shown in Table 3 are results from leveling observations. The results shown in Table 3 show that two formulations demonstrate sufficient performance versus the benchmark fluorosurfactant Zonyl® FSJ. Notably, these are formulations A and O and are both biesters of sulfosuccinates. All other surfactants and combinations suffered defects at some stage. The addition level required for adequate performance in appearance of both sulfosuccinates, Edaplan® LA 451 and Aerosol® OT-70, was 10- to 100-times greater than that of the benchmark fluorosurfactant. This is not surprising given the effectiveness of the sulfosuccinates reaching a minimum surface tension versus Zonyl® FSJ. From a practical perspective, the price of fluorosurfactants is ~10-100x that of hydrocarbon surfactants, making bi-ester sulfosuccinates, and particularly bis-tridecyl, an attractive alternative to fluorosurfactants in floor polish formulations.

Another important attribute of floor polishes is burnishing resistance. In commercial applications, floors can be burnished often and on a routine basis. Maintaining appearance and gloss is critical to a successful formulation. Gloss readings before and after burnishing using Example 3 given in Tables 3 (using Edaplan® LA 451) along with the benchmark fluorosurfactant are shown in Tables 4 an 5 and graphically in Figure 1. At 800 ppm, Example 3 yields the same initial gloss measurement as a coating prepared using 60 ppm of fluorosurfactant. After multiple burnishings, gloss readings on films prepared using Example 3 are comparable or higher than films made using 60 ppm of fluorosurfactant.

Summary and Conclusions: Certain Hydrocarbon Surfactants Perform in An SB-Based Floor Polish

A new, styrene-butadiene copolymer-based floor polish formulation is presented. Adequate performance and appearance can be achieved by the proper choice of a hydrocarbon-based wetting, flow and leveling aid. Two bi-ester derivatives of sodium sulfosuccinate, bis(tridecyl) and dioctyl, have been found suitable with the bis(tridecyl) the more versatile of the two. Results of initial gloss and gloss retention after burnishing were comparable to those results obtained using a benchmark telomer-based fluorosurfactant Zonyl® FSJ. Up to between 10 and 100 times more of the hydrocarbon surfactant was required than the fluorosurfactant. This would be expected based on the effectiveness of surface tension reduction between the two types of surfactants. The price differential between fluorosurfactant and hydrocarbon surfactant (~10-100x) makes the use of bis(tridecyl) sulfosuccinate surfactants as wetting, flow and leveling aids viable economically without the potential environmental liability of using fluorosurfactants to achieve similar performance.

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Tables

Table 1. Model floor polish formulation.

Component	Amount (wt%)
Water	45.51
Diethylene glycol monoethyl ether	5.05
Dipropylene glycol butyl ether	1.00
Tributoxyethyl phosphate	1.85
Zonyl® FSJ (30 wt% solids)	0.02
Defoaming emulsion (17 wt% solids)	0.01
Biocide (20 wt% solids)	0.09
Styrene-acrylic copolymer solution (30% solids)	1.82
Wax emulsion (35 wt% solids)	5.18
Styrene-butadiene copolymer emulsion (40 wt% solids)	39.47

Table 2. Surfactant legend.

Identification	Surfactant	Type	Supplier
A	Edaplan® LA 451	Anionic	Münzig Chemie (Heilbronn, Germany)
B	Synperonic® 91/6	Nonionic	Uniqema (Everberg, Belgium)
C	Tergitol® TMN-10	Nonionic	Dow Chemical Co. (Midland, MI)
D	Tergitol® TMN-6	Nonionic	Dow Chemical Co. (Midland, MI)
E	Tergitol® 15-S-20	Nonionic	Dow Chemical Co. (Midland, MI)
F	Surfynol® MD20	Nonionic	Air Products (Allentown, PA)
G	Dynol® 607	Nonionic	Air Products (Allentown, PA)
H	Envirogem® 360	Nonionic	Air Products (Allentown, PA)
I	Surfynol®104E	Nonionic	Air Products (Allentown, PA)
J	PolyFox® PF-154N	Nonionic	OMNOVA Solutions (Fairlawn, Ohio)
K	Modarez®X043	Nonionic	Protex International (Seoul, Korea)
L	Surfac® HT20	Nonionic	Surfachem Group Ltd. (Leeds, UK)
M	Polyethylene glycol 400 monolaurate	Nonionic	Esterchem Ltd. (Leek, UK)
N	Tegotens® SD 100	Nonionic	Evonik Degussa GmbH (Hanau, Germany)
O	Aerosol® OT-70	Anionic	Cytec Industries BV (Rotterdam, Netherlands)

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Table 3. Formulation modifications and leveling performance.

Example	Surfactant(s)	Concentration (ppm)	Leveling performance
1	A	200	poor
2	A	400	adequate
3	A	400 -10,000	good at all amounts
4	B	3000	poor
5	C	400	2nd coat did not wet 1st
6	D	400	2nd coat did not wet 1st
7	E	400	2nd coat did not wet 1st
8	F	400	2nd coat did not wet 1st
9	G	400	2nd coat did not wet 1st
10	H	400	2nd coat did not wet 1st
11	I	200	2nd coat did not wet 1st
12	D & I	400 + 200	2nd coat did not wet 1st
13	C & J	200 + 200	1st coat - slightly streaked
14	G & J	1000 + 200	1st coat – blotchy
15	K	200	leopard skin pattern
16	K & J	210 + 200	visible application marks
17	L	200	thick streaks in dried film
18	M	200	thick streaks at edges of tile
19	N	200	thick streaks in dried film
20	O	1,000 -10,000	good at 10,000 ppm

Table 4. Initial gloss measurements from formulation given by Example 3 in Table 3.

Addition level Edaplan® LA 451 (ppm)	Initial gloss (60°)
400	76
600	80
800	86
970	79
1300	65

Table 5. Gloss measurements at 60° from formulation given by Example 3 in Table 3 *vs* the same formulation using Zonyl® FSJ.

	Example 3 Surfactant					Fluorosurfactant
Addition (ppm)	400	600	800	970	1300	60
Gloss measured at 60°						
Initial	74	79	85	75	65	85
Burnish #1	58	58	64	60	59	78
Burnish #2	47	51	53	51	52	53
Burnish #3	33	43	44	41	41	37
Burnish #4	78	70[a]	62[a]	78	62[a]	64[a]

[a] Slight surfactant bloom.

Figures

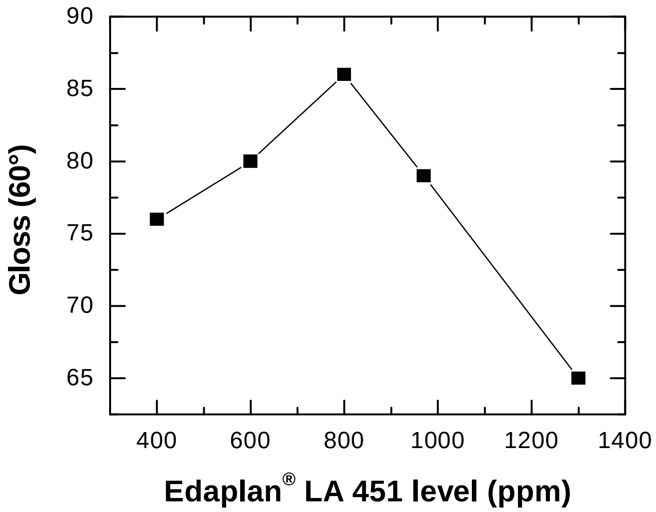

Figure 1. 60° gloss values as a function of added Edaplan® LA 451 surfactant to Omna-Glo™ 100 floor polish.