

Surface modifying additive for UV curable hardcoat

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Abstract

Hardcoats improve the durability and scratch resistance of plastics. Hardcoats are, however, susceptible to fingerprint smudge, stains and graffiti. The addition of a UV curable Perfluoropolyether additive into existing hardcoat systems can alleviate these issues. This additive is optically clear, oleophobic, hydrophobic, and provides easy-to-clean properties. Using optical and contact angle measurements, we demonstrate that UV hardcoats that incorporate the Perfluoropolyether additive have reduced fingerprint transference, easy-to-clean properties, and stain resistance than UV hardcoats without the additive.

Introduction and objectives

Hardcoats improve the durability, scratch, abrasion and chemical resistance of plastics. Hardcoats are, however, susceptible to fingerprint smudge, stains and graffiti. Anti-smudge, fingerprint resistance and easy-to-clean properties are desired in many applications including touch screen solutions and automotive interiors parts.

Radiation cure system consists of oligomer, monomers, additives and photoinitiator. The bulk properties of the hardcoat are attributed to the oligomer and monomer which make up greater than 90% of the hardcoat. Photoinitiators are utilized between 1% and 4% wt. on total formulation. There are many additives including pigments, rheology additives, defoamers, wetting and surface-active agents. A perfluoropolyether additive is a surface-active agent. The additive is compatible with many monomers and oligomer.

The addition of a UV curable perfluoropolyether additive into an existing hardcoat system can mitigate stain, fingerprint and soil by reducing the surface energy. This additive is optically clear, oleophobic, hydrophobic, and provides easy-to-clean properties. In addition, the additive also improves the slipperiness or perceived smoothness of the surface.

The literature has many “standard” artificial fingerprints. The fingerprints contain water and small amount of complex chemical mixture excreted from the sweat glands on the palms. However, as a result of contact with other parts of the body such as the face, components of sebaceous sweat including fatty acids, cholesterol etc. may be present. Moreover, reliable applying/stamping and characterizing fingerprint vary in the literature

Using optical and contact angle measurements, we demonstrate that UV hardcoats that incorporate the perfluoropolyether additive have better fingerprint mitigation, easy-to-clean properties, and stain resistance than UV hardcoats without the additive. The calculated surface energy is greatly reduced with the additive.

The perfluoropolyether additive consists of a fluorinated polymer and UV curable acrylate pendent group. The fluorinated polymer accumulates/migrates to the surface of the coating due to its high surface activity. Under UV irradiation, the acrylate pendent group polymerizes and it is anchored into the hardcoat polymer network¹.

Representative applications for these perfluoropolyether additives include nano imprinting, automotive forward lighting, anti-graffiti, resin mold release; Also consumer electronics; display protection films, electronics casing. Another potential application is flooring to mitigate black heel marks.

Experiments

Summary of test performed

- ✓ Coefficient of friction (CoF);
Friction pad speed is 200 mm/min and distance travelled is 70 mm, friction pad material is paper. Sled weight is 1.91N (ASTM D 1894).
- ✓ Goodness of feel test;
There were three (3) sets of samples. Each set has three samples. Participants were asked to rank each set separately. Within each set participants were asked to rank the samples from 1 to 3 in terms how smooth it felt to the touch (participants touched samples with Kimwipes® and not directly with their fingertips). Rank 3 is considered the worst and Rank 1 is considered the best. A total of 10 individuals participated in the feel test.
- ✓ Water contact angle (WCA), and hexadecane contact angle;
2µl drop size, 3 drops per samples, and 20 pictures per drop, on average a total of 60 data points per sample.
- ✓ Sliding angle (SA);
20µl drop of hexadecane oil. Sample was tilted at 0.5°/sec. Note the tilting angle at the point where the drop has travelled/moved a distance equivalent to its radius. The tilting angle at this point is the sliding angle.
- ✓ Permanent marker test;
Apply a straight line horizontally across sample with a black Sharpie® permanent marker, wait for minute, and wipe with Kimwipes® (4ply). If marker is not completely removed, sample failed the test. If marker is completely removed, sample passed test.
- ✓ Haze%;
Haze was measured using the BYK-Gardner HazeGard plus instrument (ASTM D1044-08).

- ✓ Easy to clean test

Stamping/Fingerprint

- Spin coat the artificial fingerprint mixture on the plastic substrate. Press against the spin-coated layer with index finger and hold for 5 sec. with approximately 500 grams of down force to transfer to finger. Take off transferred excess mixture from finger by pressing against **DublSoft®** facial tissue (for 1 sec with approximately 200 grams of down force). Now, press the index finger against the sample for 5 sec. with approximately 500 g of down force to stamp fingerprint.

Wiping conditions

- Wipe with 5 cycles (1 cycles is equal to one frontward and 1 backward movement). Measure L value with spectrophotometer of the pristine (before stamping/fingerprinting) and after wiping, and then calculate the difference (delta L, ΔL). Repeat 5 wipes and delta L measurement until 6 sets are completed (wipes 30 strokes in all).

- ✓ Adhesive tape peeling strength test;

Adhesion peel strength test, 50 mm/min, pull duration is 70 mm (This test is sort of similar to a 180 peel T-test in ASTM D3330).

Coating formulation

Table 1 Coating formulation

Materials	Mass composition (%)		
	With DAC-ST	With DAC-HP	HC_only without additive
Polyurethane acrylate*	39.2	39.2	39.2
S-7430 (OPTOOL DAC-ST) under development	1		
S-7420 (OPTOOL DAC-HP)		2	
Methyl isobutyl ketone	59.8		59.8
1-methoxy-2-propanol		58.8	
Total	100	100	100

Coating preparation and curing conditions

The coating formulation is prepared as above and applied to substrates (PC, PET, and PMMA) by bar coating with bar size # 10. This applies a wet film thickness of 1 mil. Thereafter, dry for 5 minutes at 70 °C to allow solvent to evaporate and the perfluoropolyether to migrate to the air/coating interface. Thereafter, curing was completed with a high-pressure mercury lamp at energy density of 600 mJ/cm². Coating thickness is approx. 3to 5µm.* Photoinitiator was pre-mixed with polyurethane acrylate.

A total of 9 samples were prepared. Each of the chemistries; DAC-ST, DAC-HP, HC_only were coated on PC, PET and PMMA.

Results

We performed several test on the 9 samples prepared. The summary of performance data is summarized in Table 2.

Table 2 Data summary

	PET			PC			PMMA		
	ST	HP	HC_only	ST	HP	HC_only	ST	HP	HC_only
CoF	0.103	0.173	0.428	0.122	0.184	0.48	0.12	0.163	0.438
Goodness of feel (GoF)	1.3	2.1	2.5	1.3	2.1	2.7	1.2	2.4	2.5
WCA (°)	107.7	106.6	68.5	103.1	105.5	64.8	106.1	104.7	69.8
Hexadecane CA (°)	66.2	63.4	5.8	63.9	63.5	6.1	62.5	64.8	6.7
Surface energy(dynes/cm)	14.9	15.8	40	16.5	16	42.2	16.1	15.9	39.2
SA (°)	12	8.2	--	12.2	11.1	--	12.9	10.2	--
Permanent marker test	pass	pass	fail	pass	pass	fail	pass	pass	fail
Haze%	0.89	1.04	0.88	0.23	0.04	0.08	0.02	0.01	0.01

Surface energy/WCA/OCA

The perfluoropolyether additive is both hydrophobic and oleophobic (see table 2 and figure 1) and thus it is suitable for water and oil repellency coating applications. Water and oil repellency is important for fingerprint resistance because latent fingerprint consist of water and complex chemical mixtures including acids, fat, oils and salt components.

The surface energy was calculated using the simple FOWKES method from the measured water and hexadecane contact angles. The surface free energy of a solid is a combination of the polar and dispersive components. There is a marked surface energy reduction with the addition of perfluoropolyether additive (see table 2). The surface energy for this additive is less than that of PTFE (which is 18.5 to 19 dyne/cm). Moreover, additives which consist mainly of polydimethyl siloxane have low critical surface energies, about 25-27 dyne/cm, though not as low as certain fluoro polymers^{2,3}.

CoF /Slipperiness and Goodness of Feel test

The hardcoat with DAC-ST exhibited the lowest CoF, while the hardcoat without additives showed the highest CoF. CoF is mostly independent of substrate type and strongly dependent on additive chemistry (see figure 2).

Based on the CoF data, we expected the samples with DAC-ST to feel the best in terms of slipperiness while the sample with only hardcoat (without either DAC-ST or DAC-HP) was expected to feel the worst. For each substrate type, the ranking in terms of slipperiness from best to worst should be in this order; DAC-ST>DAC-HP>> hardcoat only. The goodness of feel test confirmed what we expected (see figure 3 below). Overwhelmingly, majority of test participants ranked DAC-ST as the best in terms of slipperiness.

Various performance properties like coefficient of friction, slipperiness, surface energy are related and are attributed to perfluoropolyether additive. There is some empirically correlation between these properties. For example, lower surface energy surfaces also have lower coefficient of friction. Coefficient of friction is a measure of the friction forces between two materials or surfaces in contact. Lower surface energy surfaces typically exhibits lower adhesion energy or lower attraction.

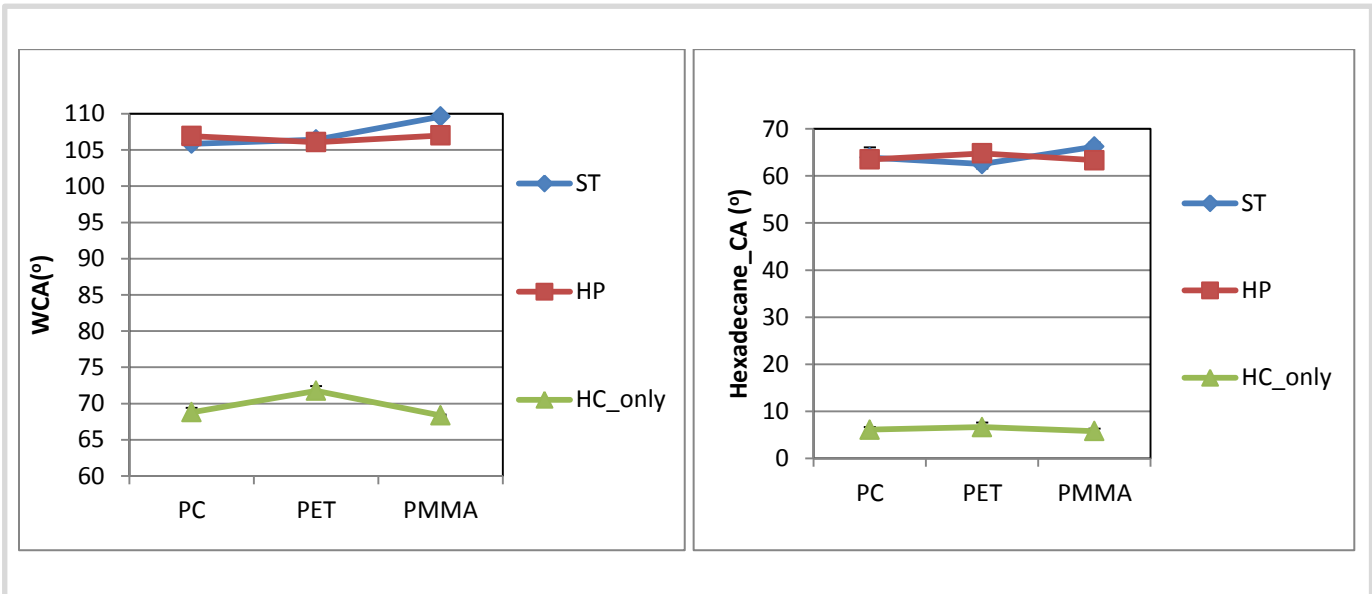


Figure 1 Water and Hexadecane contact angle of various coated substrates

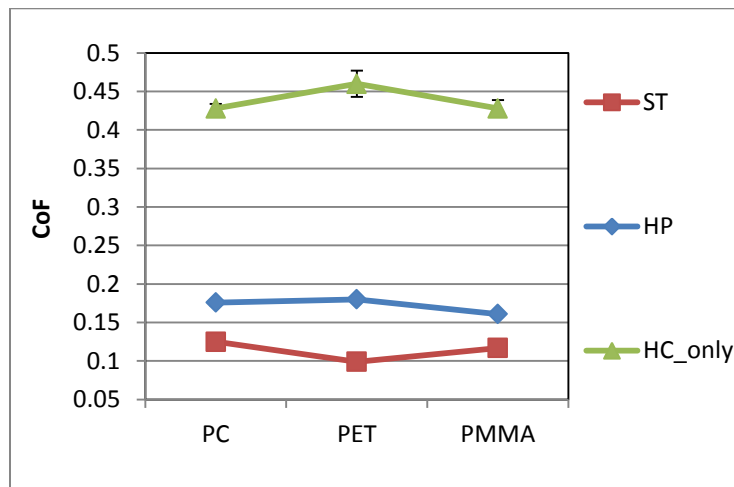


Figure 2 CoF of various coated substrates

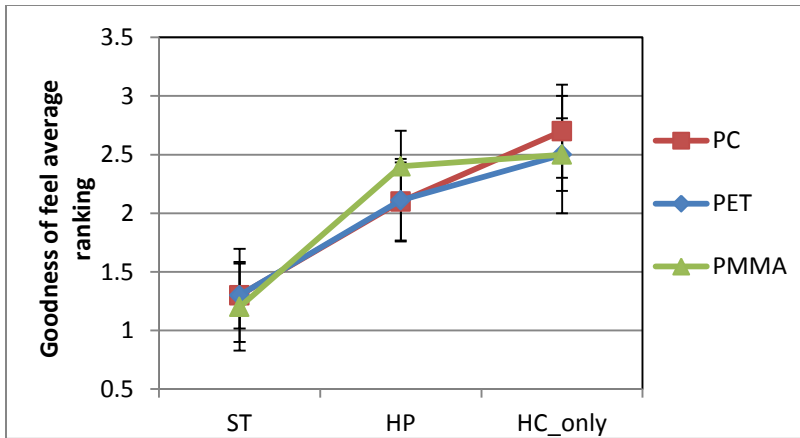


Figure 3 Goodness of feel test

Adhesion strength tape peel test

Release properties are important in mold release application. The tape adhesive strength on HC_only shows the strongest adhesion (See figure 4). The adhesive “wets” the high energy surface of the HC_only. DAC-ST shows the smallest tape adhesion strength. As mentioned earlier, the lower adhesion properties are attributed to lower surface energy. In general, higher surface energy results in greater adhesion strength. There is a linear empirical correlation between adhesive strength, coefficient of friction and goodness of feel test data.

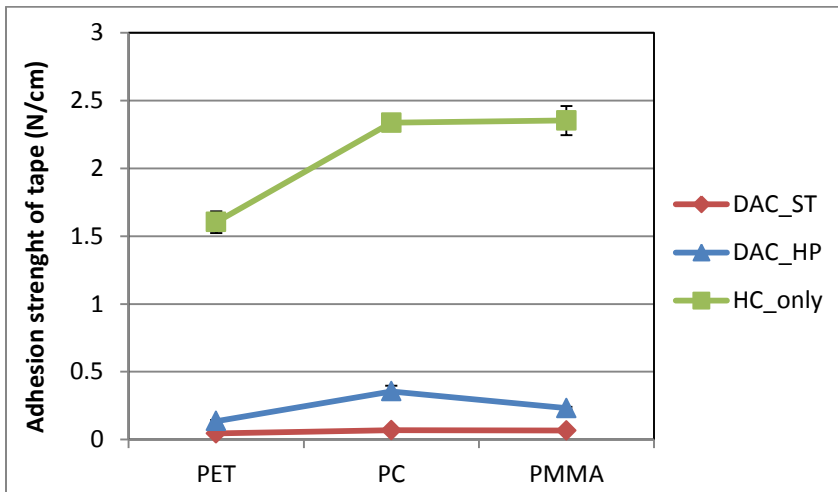


Figure 4 Adhesion strength of tape (Scotch® Magic™ Tape)

Cleanability of fingerprints

The residual fingerprint on touch-enabled electronic devices, stainless steel appliances and piano-black surfaces in automotive interior parts are unsightly. Perfluoropolyether helps to mitigate fingerprint. There are two aspects to easy-to-clean; one is fingerprint/soil mitigation or resistance, which is a quantitative measurement of fingerprint transference to the surface; the other is cleanability or wipability i.e. how easy it is to clean or wipe off the transferred or deposited material or soil.

Microscopic view of the fingerprints ridges shows the fingerprint de-wets into “micro-beads” on hardcoat with the perfluoropolyether additives. Conversely, the fingerprint ridges on HC_only are not well defined, it appears that the fingerprint spreads and coalesces into bigger globule due to wetting (See figure 5). The micro-bead is an indication of the fingerprint mitigation.

We used the change in L (ΔL) to measured cleanability (L after wiping compared to the pristine-normalized to zero, 0). In general, we noticed that at any given wipe cycles, L value of the coating with the perfluoropolyether additive is closer to zero than hardcoat_only. The perfluoropolyether additive show better cleanability and better fingerprint mitigation. The data suggest that DAC-HP has a slightly better cleanability than DAC-ST. (See figure 6). Moreover, DAC-HP has a lower sliding angle than DAC-ST, which hints that the liquid has a lower adhesion on DAC-HP (See table 2). The small sliding angle is important in self-cleaning application. Figure 7 shows pictures of the wiped fingerprint after 30 wipes. HC_only clearly shows residual fingerprint on the wipe patch, while the wiped patch for DAC-HP and DAC-ST is ostensibly clean.

Both DAC-ST and DAC-HP are also stain resistance; a black permanent marker stain was easily wiped off with tissue paper. The permanent marker stain was not removed from HC_only sample after wiping (See table 2). Also the marker beads up on DAC-ST and DAC-HP, but “wets” HC_only. The permanent marker test is a qualitative indicator of oleophobicity and hydrophobicity.

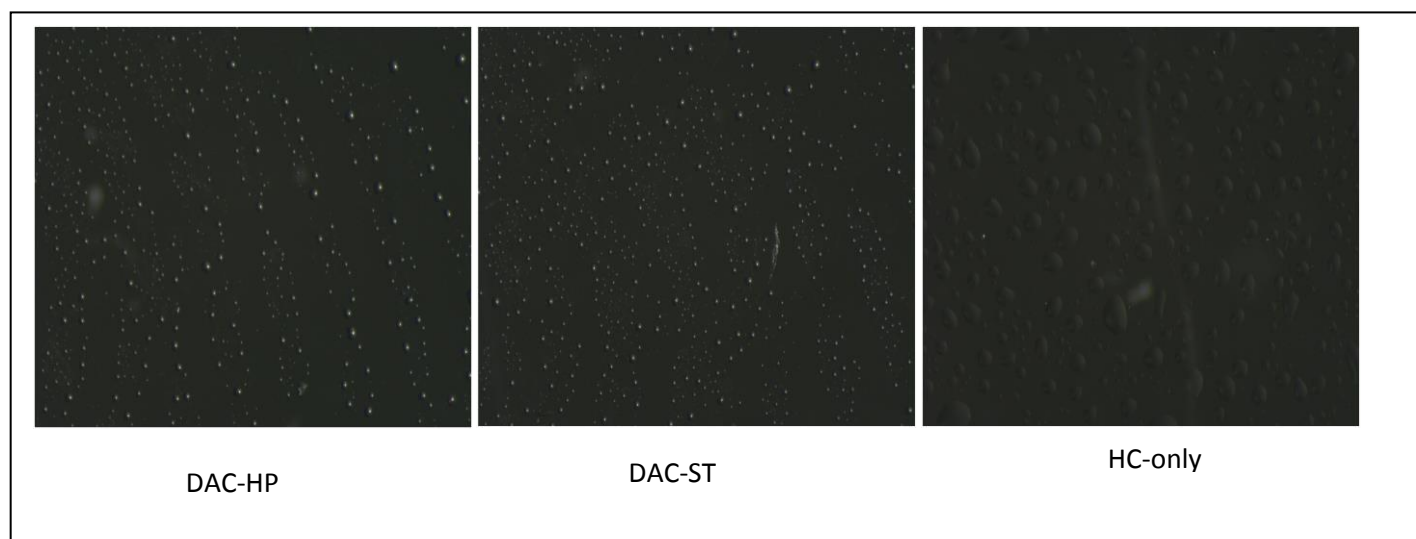


Figure 5 Fingerprint ridges under microscope, 40X magnification

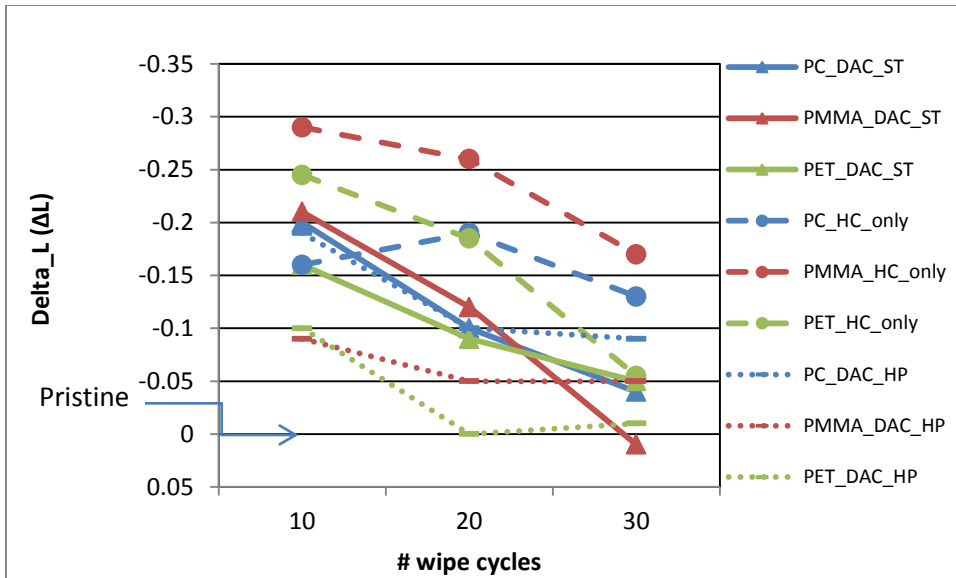


Figure 6 Cleanability data; Delta_L (ΔL) as a function of # wipe cycles

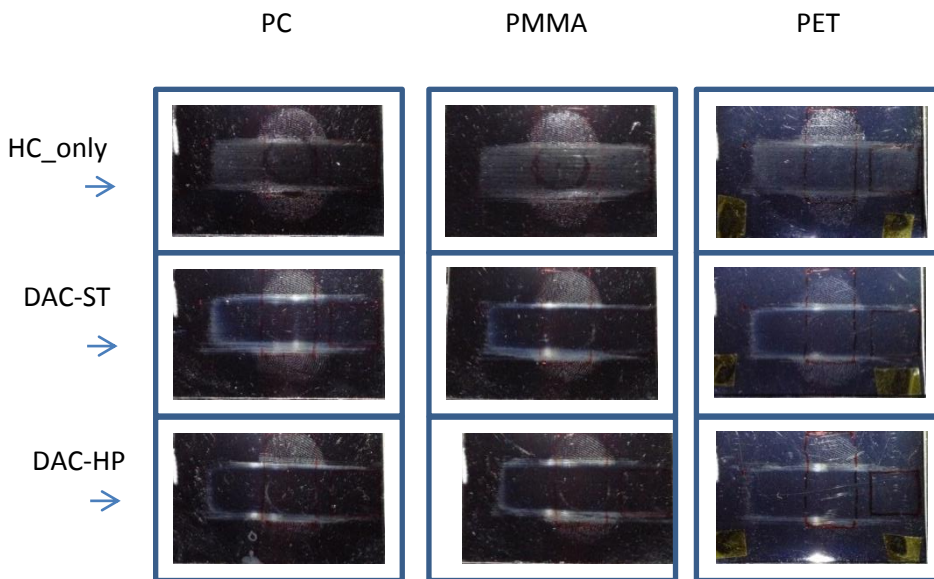


Figure 7 Pictures of fingerprint after wiping with tissue

Haze and transmission

Among PET, PC and PMMA coated samples, the PET coated film have most haze, and while the PMMA coated samples have the lowest haze. The additives (ST, HP) apparently have no significant impact on total transmission. The change in transmission compared to the hardcoat only is less than 1% (See Table 2 for haze data).

Conclusion

The micro-bead in the fingerprint ridges indicates that the perfluoropolyether additive mitigate fingerprints. Moreover, the perfluoropolyether additive improves the cleanability and stain resistance properties of hardcoat. Both artificial fingerprint and black permanent marker were easily wiped off the hardcoat containing the additive. The additive also results in marked reduction in surface energy of the hardcoat.

Furthermore, the subjective goodness of feel test correlates well with coefficient of friction data. The perfluoropolyether additive is optically clear and has no significant adverse impact on haze and transmission of the hardcoat.

References

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