Advancements and Challenges in "Easy-to-Clean" Coatings

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Abstract

Electronic touch screens are no longer just a part of communication devices. They are now key components in automotive interiors and home appliances. As such, the demand for anti-fingerprint technology has increased dramatically. When you also consider the ramped-up development in autonomous vehicles, the need for dirt repellent hard coats is no longer an aesthetic want, but a critical safety need. The challenge to develop and evaluate "Easy-to-Clean" hard coats is a pressing issue in multiple coating markets. This paper will discuss some coating technologies, the challenge of quantifying the technology, as well as unmet needs in these areas.

Introduction

Coatings have many functions in today's world. Some are simply for aesthetics, while others provide various degrees of protection. As technology advances, new niches are arriving that will require protection not only of the substrate, but of the users themselves. Easy to Clean coatings can play a role in both aesthetics and protection.

Easy to clean coatings (EAC) can refer to many different properties: anti-graffiti, anti-fingerprint, anti-ice, or dirt-repellant for example. The definition can be interpreted as: nothing sticks to the coating, reduced dirt pick up, or the coating can be fouled, but the fouling cleans off with little to no effort. Applications for these types of coatings are abundant and continue to grow. As mentioned previously, some are merely for aesthetic purposes – anti-graffiti for barrier walls and anti-fingerprint for appliances and touch screens, while others are necessary for safety – anti-ice for aerospace.

A newer but ever-growing area of interest is autonomous vehicles. The level of autonomy can vary from 0 to 5. L0 requires the driver to perform all functions. L1 and L2 have limited autonomy and the driver must be involved. L3 only requires intermittent driver attention. With L4, a driver is not necessary, but one still needs to be present and can override the autonomy if needed. L5 would be a truly self-driving car – it makes all the decisions and actions based on its sensors and processing. For vehicles on the road today, the majority lies in the 1-3 range.

Advanced Driver Assistance Systems (ADAS) are being included in almost every make and model of vehicles on the roads today. This system includes such technologies as adaptive cruise control

(ACC), autonomous emergency braking (AEB), and lane-keeping assist systems (LKAS). All new cars in the United States are required to have back up cameras. Other forms of sensors are radar, and less frequently, Light Detection and Ranging (LIDAR). For optimum safety, vehicles will need a blend of these technologies, called Sensor Fusion. Examples and details of each are listed in *Table 1*. To improve reliability, lenses for these sensors are prime candidates for EAC coatings.

Table 1: Sensors Used in Automotive Sector Today

Type of Sensor	Mode	Examples	Advantages	Disadvantages
Camera	Visible light; some Infrared	Surround view systems; driver monitoring systems	Low cost	Ineffective in bad weather
Radar	Short Range: 24 GHz Long Range: 77 GHz (newer)	ACC; AEB	Not effected by weather or darkness	Limited resolution (especially short range)
LIDAR	Infrared: 905 nm (main wavelength) and 1064 nm	True autonomous vehicles	Very detailed information; longer range; more accurate	Costly; car to car interference

Determining Easy to Clean Properties

OEMs (Original Equipment Manufacturer) know what they want; the issues have been in determining how to know when they get there and at what cost. What is the best way to simulate real life scenarios? Are there coating properties that can be measured that will indicate the desired properties? Can all these attributes be achieved with the same formulation techniques?

When talking about EAC coatings, two properties typically enter the conversation: contact angles and surface texturing. It is obvious that a low gloss coating is better at hiding fingerprints than a high gloss coating. A fingerprint can be present on a low gloss coating, but due to the unevenness of the surface, the fingerprint is not visible to the human eye. This disruption of the pattern makes fingerprints hard to detect. However, there are reasons why a low gloss coating will not work for an EAC application; certain transparency and haze criteria may be mandatory for viable use of the product.

If "macro-texturing" cannot be used, there is an option to use nano-texturing. This technique has become very successful in many applications. The coatings are very thin, and the texturing is not visible to the naked eye; however, there is a disruption in the surface that makes a fingerprint harder to detect. These coatings are very effective at "anti-fingerprinting", but other properties may not be sufficient for all markets, such as weatherability, or chemical and scratch resistance.

Contact angles can be used to classify coatings. An oleophobic coating would have a contact angle with hexadecane greater than 60°. If a coating is oleophobic, it will repel oils. Since fingerprints can have a high oil content, this property can improve the ability of a coating to minimize the appearance of fingerprints. A coating with a water contact angle of >110° is deemed hydrophobic and

>150° would be superhydrophobic. The higher the contact angle, the less likely water will be able to cover the surface; causing beads of water to form, rather than a continuous film (hydrophilicity). If a coating has hydrophobic and oleophobic properties, it can be called omniphobic and not allow oils or water to form on the surface. Since foreign materials cannot form continuous layers on the coating, it is believed that the higher the water and oil contact angles, the better the cleanability of the coating.

When working with the automotive industry, whether interior or exterior, longevity of the coating and its properties are a critical focus. For EAC coatings, it has been proven that exposure to UV radiation and moisture can have a negative impact on the ability of the coating to maintain its cleanability. *Table 2* lists contact angles, measured with a FTÅ 400 Dynamic Contact Angle Analyzer, of a typical UV curable hard coat, "Hard Coat 1", with no EAC additive and three commercially available additives. Contact angles were measured initially as well as after a 36-hour hydrolysis test. From this quick screening, these additives show a bigger effect on oleophobicity than on hydrophobicity. The data also shows that permanence of the additive is not guaranteed. Because many additives on the market today come at a higher price, one needs to ensure that the added coating cost will be worth the properties it provides. If a coating is only expected to last 6 months or less before it needs to be replaced, can a lower priced formulation provide the necessary protection?

Table 2: Different Additives in Hard Coat 1

Additive	**Water Contact Angle (initial)**	**Water Contact Angle (post hydrolysis)**	**Hexadecane Contact Angle (initial)**	**Hexadecane Contact Angle (post hydrolysis)**
None	95°	80°	<10°	<10°
A	92°	82°	57°	57°
B	104°	93°	46°	44°
C	109°	105°	56°	50°

Of course, not all formulations are created equal. An additive may dramatically raise the contact angle in one system, but a slightly different chemistry may show no effect *(Table 3)*. Like most formulations, additives and chemistries will have different synergistic effects and proper screenings and testing is required to ensure the optimum match.

Table 3: Additive A in Different UV Curable Coatings

Coating	Water Contact Angle w/o Additive A	Water Contact Angle w/ Additive A
2	80°	89°
3	72°	108°

Intuitively, contact angles should influence cleanability, but is this true in reality? Some methods to determine how easy it is to clean a coating have been introduced. The following discussion pertains to optically clear hard coats. The general procedure would be to measure transparency and haze on a coated panel / part before and after dirt application, remove dirt and re-measure transparency and haze. The variables to this test are: what to include in the dirt mixture; how to apply said mixture; how to clean the coating.

This process can be expanded upon by starting with the “dirt mixture”. By evaluating road “grime”, it has been determined that the dirt components can include: silica, carbon dust, sodium carboxyl methyl cellulose (NaCMC), salt, dish detergent (as a surfactant), and/or water. The dirt can be spray applied (if aqueous) or shaken onto the panel. The time and conditions that the dirt remains on the panel can range from 1 to 24 hours at room temperature or up to 120°F. Also, there does not seem to be a standard cleaning method. As such, various techniques have been tried to determine an optimum method that would also be viable in a real-world scenario. *Table 4* shows differences in % Transparency (higher being more desirable) and % haze (lower the percentage, the better the clarity of the coating) depending on the cleaning method. Again, “Hard Coat 1” is a traditional acrylate formulation with good exterior durable properties. “Hard Coat 1C” is the same coating, but with “Additive C” (as mentioned in *Table 2*).

Table 4: Effect of Different Cleaning Techniques on Transparency and Haze

	% Transmission			**% Haze**		
	Without coating	Hard Coat 1	Hard Coat 1C	Without coating	Hard Coat 1	Hard Coat 1C
Initial Values[1]	88.5	88.9	88.7	0.28	0.21	0.37
Post Dirt Application[2]	*65.6*	*64.2*	*77.4*	*41.6*	*44.6*	*11.5*
Post Water Cleaning[3]	78.8	72.4	85.3	7.07	15.1	2.12
Post Air Cleaning[4]	*84.2*	*86.4*	*88.1*	*15.4*	*8.04*	*1.97*
Post Wiping[5]	79.7	87.8	88.7	29.8	2.19	0.78

[1]Transmission and Haze measured via Byk Gardner haze-gard plus; substrate: polycarbonate

[2]Applied by placing panels into a plastic bag with a dirt blend of silica, carbon dust, NaCMC, and salt. Bag was shaken for 30 seconds before panel was removed

[3]Panels held under Cold water with very low pressure for five seconds

[4]Panels exposed to five seconds of compressed air

[5]Panels wiped two times with a dry cloth using moderate pressure.

All panels started with similar Transparency and Haze values; however, Hard Coat 1C, with the additive, showed lower dirt pick up, as evidenced by the much lower haze readings. The modified coating also recovered more than the unmodified version or the uncoated panel. A physical removal did prove to be the most effective cleaning method for the coated samples but had worse haze values on the uncoated polycarbonate panel due to the cloth scratching the substrate. However, in an actual application with sensors for the automotive industry, if the lens relied on a physical wiping to remove residue, this would be harder for OEMs to incorporate into the design of the sensor. There are some automotive systems in test today that do utilize spritzes of water / cleaning solution during the use of the vehicle to keep the lenses clean. If puffs of air could be a more efficient cleaning mechanism, depending on where the sensor is located, could the air displacement from the moving vehicle be enough to dislodge the debris?

Improving Cleanability

Since Coating 1C did perform well in a cleaning test situation, but failed to reach the requisite contact angles to be considered hydrophobic or oleophobic, other modifications were tested to see if these values could be raised and if they would have any effect on the cleanability of the coating.

Formulation changes, as well as processing studies were able to give increases in contact angles. With the right adjustments, initial water contact angles reached as high as 111° and hexadecane contact angles of 63° (109° and 56°, before modifications, *Table 2*). The permanence of these formulas was also quite good, seeing only a decrease to 109° and 61° (105° and 50°, before modifications, *Table 2*) respectively. Comparison of the results of the formula / process optimization to Hard Coat 1C are listed in *Table 5*. It is interesting to note, that although similar, the dirt pick-up resistance in the modified formula is not as good as previously measured. Also, the water cleaning method gave lower haze values than the air cleaning method with this version. This could be an indication that the increase in hydrophobicity did indeed improve the cleanability of the hard coat. Further testing needs to be conducted to ensure repeatability, validity, and applicability of the test results.

Table 5: Cleanability Results of Improved Formulation

	% Transmission		**% Haze**	
	Hard Coat 1C	Hard Coat 1C (optimized)	Hard Coat 1C	Hard Coat 1C (optimized)
Initial Values[1]	88.7	89.1	0.37	0.4
Post Dirt Application[2]	77.4	83.7	11.5	13.2
Post Water Cleaning[3]	85.3	88.8	2.12	1.27
Post Air Cleaning[4]	88.1	89	1.97	2.17

Conclusion

Along with advancements in autonomous vehicles, the interest in Easy to Clean coatings continues to increase. Despite this interest, standard tests or actual coating requirements have yet to be developed and communicated. Coatings can be developed to hit the target hydrophobic and oleophobic values, but does this really make them easy to clean coatings? Many questions remain as to the relevance of the existing tests and the properties of the coatings that give the best cleanability properties. Because of the complexity of the technologies, additional test methods and formulas need to be evaluated to determine what is the best way to predict cleanability and maintain permanence of the coating properties. This may take multiple disciplines coming together to devise a smart, reproducible and accurate technique to aid in further development and eventual commercialization of Easy to Clean coatings.