Self-Cleaning Coatings

Final Report

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Abstract

Under certain conditions, military coatings can become soiled or contaminated by oil or water borne chemical agents, or oily/sooty matter from engine exhaust. Protective coatings that are both durable and self-cleaning are desirable, especially for hard to reach locations. Super-amphiphobic coatings with high surface roughness and low surface energy maybe appropriate for beading aqueous and oily liquids, however, rough surfaces tend not to be durable, can trap surface contamination, and contact angle hysteresis can increase the tilt angle required for the beaded liquid to roll off of the surface (a process by which the rolling liquid drop carries away surface contaminants). For these reasons a smoother surface is preferred. Fluorinated particles can be used for reducing the coating's surface energy but they must be functionalized in order to increase bonding to, and formation of a durable coating. In this report a new approach to fabricate self-cleaning coating surface is investigated, where different types of particles are functionalized in a fluidized bed and dispersed into a commercial polysiloxane coating resin. These coatings were evaluated in regards to their hydrophobicity, oleophobicity and self-cleaning efficiency. The modified paint exhibited similar hydrophobicity, higher oleophobicity, and some improvement in self-cleaning efficiency than the original paint.

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1. Introduction

Normal solid surfaces are wetted by liquids such as water and oil. In many cases, surface wetting is undesirable due to the fact that the liquids may largely deteriorate the functionality of the surface, or cause unwanted effects. For example, evaporation of liquid droplets could leave behind chemical or dirt residue on the surface; soot and oily deposits may contaminate the surfaces and they are normally hard to remove without scrubbing.

Under certain conditions, military coatings can become soiled or contaminated by oil or water borne chemical agents, or oily matters from engine exhaust. Surface coatings that are durable and self-cleaning are desirable. This kind of coating has to be both hydrophobic and oleophobic so that contaminants won't adhere to the coating surfaces and will come off easily.

There are two challenges in developing these materials:

1. It is difficult to select the functional materials that possess both hydrophobicity and oleophobicity. The surface tensions of oils (including organic solvents) are smaller than water, so a surface that repels water is not necessarily oil repellent. However, an oil repelling surface has to be water repelling in the first place, and

2. It is challenging to properly incorporate oleophobic materials into a coating resin system and make the coating mechanically durable, due to a lack of functional groups on oleophobic particles for chemical bonding.

Many attempts have been made by researchers to produce oleophobic surfaces on a variety of solid substrates in the past decade. Shibuichi etc[1] prepared a super oil-repellent surface using anodically oxidized aluminum surface treated with fluorinated monoalkyl phosphates. The contact angle of rapeseed oil on this surface reached 150º. Yabu etc[2] formed hydrophobic and lipophobic surfaces of fluorinated polymers by a water-assisted self-assembling process which produced a honey-comb-patterned film. Li etc[3] treated ACNT (aligned carbon nanotube) films formed on quartz surface by using hydrolyzed heptadecafluorodecyltrimethoxysilane. The fabricated surfaces showed "amphiphobic" properties. Many other researchers have reported their amphiphobic surfaces[4-9] as well. All the above reported research employed fluorinated polymers as the top surface, or fluorinated organic agents to treat the top surface. Use of fluoro-containing materials to produce oleophobic surfaces is a "must" approach concluded by many of the above-mentioned researchers. Furthermore, all of the current arts in producing super amphiphobic surfaces require rough base surfaces, which is another "must" for higher oil contact angles.

The requirement of this project is for the formulation of a durable self-cleaning military coating. Under certain conditions, military coatings can become soiled or contaminated. Examples of the types of contamination could include soot and oil deposits from engine exhaust, or contamination from oil or water borne chemical agents. The UWO Particle Technology Research Group has been conducting hydrophobic coating research for years in an approach where functional (hydrophobic) particles are incorporated into coating systems to generate hydrophobicity[10]. It was proposed in the research proposal of this project that different types of functional particles would be tested and a formulation and process would be developed for the target purpose.

On the other hand, it was pointed out by some researchers[11,12] that the (water or oil) contact angle hysteresis plays an important role in water or oil repellence, which in turn is affected by the roughness. A rough hydrophobic/oleophobic surface leads to a higher contact angle, but may also result in a higher contact angle hysteresis, which would reduce the water or oil repellence. Being durable is one of the basic requirements for the coating, the finish has to be a smooth one, otherwise it won't possess the mechanical durability and also the contaminants will stay in the surface structure, according to our experience.

Another requirement of this project is that the developed coating systems shall be based on two current military coating systems. One is MIL PRF 2635D, silicone alkyd, type 2, class 2, grade C, US Federal colour standard 595B colour 26480, or International Interlac 1 or Amercoat 7229C. The second coating system shall be Mil-DTL-64159 type II, US Federal colour standard 595B colour 34094.

In this research, functional particles having the potential to provide amphiphobicity for coatings were screened in preliminary experiments. Military coatings were sourced and finally one coating, PSX-700, was available and obtained for this project. Selected functional particles were incorporated into the coating at different loadings and the resulting finishes were tested for hydrophobicity, oleophobicty and self-cleaning effect.

2. Study of self-cleaning coating surfaces with incorporated functional particles

2.1 Methodology and experimentation

2.1.1 Methodology and materials

2.1.1.1 Methodology

The basic methodology in this research is to incorporate functional particles, which are both hydrophobic and oleophobic, into the military coatings to enhance its repellence to dirt and oily contaminations. In our previous work, we have developed a few types of functional particles for producing hydrophobic coatings.[10] However, for a coating that also repels oil, it must contain fluorinated polymer or fluorinated organic agent. The candidate particles were therefore selected from those few types of particles of fluorinated polymers. Included in the group of candidates are:

Particle A: a single component fluorinated polymer, mean particle size 35 µm

Particle B: a single component fluorinated polymer, mean particle size 4 µm

Particle C: a compound of fluorinated polymer and polypropylene, mean particle size 9 µm

Due to the fact that all three types of particles have low surface energy and almost no bonding sites available for cross-linking, they would neither properly disperse into nor bond to the coating system. The direct result would be poor finish quality and deteriorated mechanical properties. Hence one of the key challenges of this research is to develop a method to modify the particle surfaces to make them dispersible into and bondable to the resin system.

A particle surface pre-treatment was employed in this research to activate and ensure proper dispersions of these functional particles into the coating system. It is anticipated that the particle type, loading ratio, and dispersion will all affect the final self-cleaning and mechanical properties of the coating.

We contacted the suppliers of the recommended military coatings. However, none of them were available. Instead, one of the suppliers recommended and provided PSX-700 which is a replacement of Amercoat 7229C. PSX-700 is a weatherable epoxy based polysiloxane coating. What the supplier could provide is the final product of PSX-700 and the corresponding hardener and thinner. It was impossible to acquire a sample that does not include filler. Therefore, removal of the filler from PSX-700 was the first required in order to make space for the addition of our functional particles in the system.

2.1.1.2 Materials

PSX-700 paint, hardener and Amercoat 911 thinner used in this project were provided by PPG Protective and Marine Coatings Company.

Particles A and B were single component PTFE fluoropolymers with D50 diameters of 35 µm and 4 µm respectively. Particle C was a PTFE-Polyethylene compound of diameter 9 µm.

Aluminium alloy panels (Q panel A-2-3.5, measuring 2*3.5*0.025 inches) and steel panels (Q panel R-36-I, measuring 3*6*0.025 inches) were used for sample panel spray.

2.1.2 Experimentation

The functional particles A, B and C are to be added to the commercial paint PSX-700 to increase its hydrophobicity and oleophobicity. Included in the experiments are following procedures: 1) Removing the filler from the paint; 2) Modifying the functional particle surfaces to make them dispersible and bondable to the resin system; 3) Incorporating the particles into the coating system and 4) Applying the modified PSX-700 to sample panels and then performing preliminary self-cleaning tests and mechanical property tests.

2.1.2.1 Equipment

Particles were pretreated to functionalize the particles for proper dispersion and bonding. A centrifuge, model 614 made by Drucker Company, was utilized to remove the filler from PSX-700 paint. A high speed stirrer and a magnetic stirring apparatus were used to mix the functional particles into the PSX-700 paint. A ball mill (Cardco Company, USA), was used for final homogenizing the particles with the paint. A vacuum suction flask was used to volatilize the extra thinner from the mixtures.

2.1.2.2 Procedures

Removal of filler from PSX-700

The original PSX-700 paint was diluted by 50 vol % of thinner. The diluted paint was transferred into the centrifuge tubes and centrifuged for 10 min. The upper clear part (the resin and solvent) of the tubes was poured into a vacuum flask, while the precipitate (filler) from the bottom of the tubes was collected and put into a container. After all the paint was done, the filler was rinsed using the thinner and centrifuged for a few more times. The rinsing thinner was also collected in the vacuum flask until the whole rinsing-centrifuging process was done.

The vacuum flask was then connected to vacuum pump to vaporize the excessive thinner. Measure the solid percentage of the filler-removed paint by baking a small sample in an oven.

Surface modification of the functional particles

The dispersability of functionalized particles A, B and C was evaluated by comparing it to the dispersability of untreated particles, in the filler-removed paint.

The dispersibility was tested by dispersing the treated particles in the filler-removed paint (refer to section "Incorporation of particles with filler-removed PSX-700") and then filtering the dispersion through a nylon screen after being diluted (for ease of filtration) by two times (volume) of thinner. The "oversize particles" (agglomerates) on the screen were rinsed to wash off residual resin with two times (volume) of thinner, before being dried up in an oven at 60˚C for an hour. Finally the weight of "oversize particles" was weighed. It was our criteria for an acceptable dispersibility that at least 99% of the particles incorporated in the filler-removed paint went through the screen (100 mesh for Particle A; 320 mesh for Particle B and 160 mesh for Particle C) was achieved through the pre-treatment. For untreated particles, more than 90% of the particles won't be able to go through the screen.

Incorporation of particles with filler-removed PSX-700

Particles A, B and C were added into the filler-removed PSX-700 respectively to produce modified paint samples for testing. The mixture was transferred to the ball mill which was then run for 8 hours to fully disperse the functional particles into the paint. Due to the limited capacity of the ball mill, multiple batches of ball mill dispersion process were carried out to make 1 litre of the final paint.

Filtration of the modified paint

In order to ensure a seeds-free final paint, the modified paint was filtered through a 270 mesh nylon screen to remove any undispersed functional particles and contaminants.

Addition of hardener and thinner

Before applying the paint samples to panels, hardener at a weight ratio of 26.2 g per 100 g of the filler-removed PSX-700 has to be added in the system and quickly mixed by hand. This ratio is equivalent to the suggested 1:4 (v/v) ratio for the original paint PSX-700. The hardener to filler-removed paint ratio was calculated from following method:

1) The density of the curing agent is 1.003 g/ml.

2) 1200 ml of original paint was used to make 1149 ml of the filler-removed paint (the loss of resin during filler-removing process was neglected).

3) The weight of the filler-removed paint was found to be 1146.5 g. The density of the filler-removed paint was 0.998 g/ml.

3) The curing agent needed for the 1146.5 g of filler-removed paint was the same as that needed for 1200 ml of original paint, which was 300 ml, or 300 ml x 1.003 = 300.9 g.

4) Then the weight ratio of hardener to the filler-removed paint was 300.9/1146.5 = 26.2.

For the hardener to modified paint ratio, it would vary along with the amount of functional particles added in. Take the 15% particle concentration as an example, it was calculated as follows:

1) The solid concentration of the filler-removed paint was measured and it was 80.1%.

2) For every 100 g of the filler-removed paint, 26.2 g of hardener was needed to cure it.

3) Assuming X g of particles were added in the 100 g filler-removed paint to make a dry-weight concentration of 15%, i.e.:

$$X / [X + (100 \times 80.1\%)] = 15\%$$

Then X = 14.1 g.

4) The weight of the modified paint was 100 + 14.1 = 114.1 g.

5) Therefore, the hardener to modified paint ratio was 26.2/114.1 = 23.0.

Panel preparation

Paint samples with different functional particles and various particle loadings were then applied to aluminium alloy panels of 2 x 3.5 x 0.025 inches for initial testing. Thinner was added to adjust the viscosity of paints for proper application, either using Mayer bar (R. D. Specialties, USA) or sprayer. For Mayer bar application, about 7% (volume of the paint) of thinner was added in to adjust viscosity for best application. The best formulation was used to spray on steel panels of 3 x 6 x 0.025 inches for further testing. When sprayer was utilized, about 50% (volume of the paint) of thinner was added in to make the paint sprayable. After applying paints to the panels, they were allowed to dry to touch at room temperature before being exposed to the curing condition of 60°C/1 hour.

In total 20 aluminium alloy panels were prepared for initial testing and 3 steel panels were prepared for further testing, as listed as follows:

For initial testing:

Selection of particle type and loading ratio:	12 aluminium panels
Adhesion tests:	2 aluminium panels
Self-cleaning tests:	6 aluminium panels

For further testing:

Hydrophobicity/oleophobicity tests and self-cleaning tests:	3 steel panels

Initial testing

1. Selection of particle type and loading ratio

Selection of the best particle type out of the three candidate functional particles A, B and C was conducted by comparing the coating properties. Coating surface quality, hydrophobicity and oleophobicity were considered when choosing the best functional particles.

2. Adhesion tests

Impact testing was conducted using an Elecometer 1615 Variable Impact Tester to quickly determine the adhesion of the modified paints in comparison with the original PSX-700.

3. Cleaning efficiency tests

The cleaning efficiency testing should be performed following the military standard MIL-PRF-85570E.[13] It was realized that we did not have all the required equipment and materials to fully comply with the standard when performing the cleaning efficiency testing. However, we required some initial results so that we could modify our formulations/processes for further optimization. Therefore, we used a procedure that mainly follows the MIL-PRF-85570E standard but with some alternative steps adopted.

Substrate panels

Standard requirements

a. Aluminum alloy panels, measuring 6*2.5*0.02 inches(15.2*6.4*0.05cm) shall be prepared.
b. At least three panels shall be used for each product tested and control formulation.
c. The set of panels used in one test run shall have the same gloss readings as those used for the control run. The gloss shall be measured by 85 degree reflectance and shall be in the range of 2-5 gloss units.

What we have used

For initial testing: Aluminum alloy panels, Q panel A-2-3.5, measuring 2*3.5*0.025 inches.

For further testing: Steel panels, Q panel R-36-I, measuring 3*6*0.025inches.

The gloss readings satisfied the requirement of the standard.

Soil Preparation

Standard requirement

a. Hydraulic fluid should satisfy MIL-PRF-83282, and grease oil should meet MIL-G-21164.
b. The hydraulic fluid soil should be homogenized with a high speed Cowles type dispersator or other high shear mixer for 15 minutes.
c. The molybdenum disulfide grease soil shall be blended by hand then with a mechanical grease worker for 15 minutes.

What we have done

Hydraulic liquid soil was prepared by blending 1:10 (weight ratio) carbon black and hydraulic liquid first by hand, then in a ball mill running 8 hours to get the uniform soil.

Grease soil was prepared by blending carbon black and grease at 1:10 weight ratio by hand.

A high shear mixer was used instead of the Cowles type disperator to prepare the hydraulic fluid soil, but the soil wasn't uniformly mixed in. So a ball mill was used.

Application of hydraulic fluid and grease soils

Standard requirement

a. Hydraulic fluid soil shall be uniformly applied to the whole surface of the panel.
b. 0.12 g grease soil was applied center across the panel in a band 1.5 inches wide and perpendicular to the long dimension of the panel, using hog bristle brush, 12 cycles, 1000 g force.
c. The brush should be Gardner WG 2000B, made by Paul N.Gardner Company.

What we have done

Using a soft polyester brush, the coated surface of a test panel was gently applied with the hydraulic fluid soil. Excessive hydraulic fluid soil was removed by covering the test panel with folded absorbent tissue and exerting pressure by rolling over the tissue with a five-pound rubber cylinder. This procedure was repeated twice.

Using a 0.5 inch polyester brush, grease soil was applied center across the panel in a band 2 centimeter wide and perpendicular to the long dimension of the panel. The soil was brushed on the central band until it was uniform.

Each soiled panel was baked at 221±2°F for 60 minutes, then cooled down to room temperature and used within four hours.

Record the soiled lightness value as L_s.

As smaller size of panels were used in the test, the band width was changed from 1.5 inches to about 2 cm, and the amount of grease soil on the band was changed according to the weight per unit area of grease soil.

A polymer brush was used instead of a hog bristle brush.

Application of wire rope lubricant

Mineral oil was used to replace wire rope lubricant suggested by the standard. It was sprayed onto the test panel and was wiped back and forth immediately using a piece of non-abrasive cleaning pad to achieve a uniform soil in the center of the panel. The soiled test panel was baked at 221±2°F for 60 minutes then cooled down to room temperature.

Preparation of Stock solution

Standard requirement

a. A 10-grain hard water stock solution shall be prepared by dissolving 0.2 g analytical reagent acetate monohydrate, 0.14 gram of analytical reagent grade magnesium sulfate heptahydrate in one litre of D. I. water.
b. Cleaning compound: as required by MIL-PRF-85570E.

What we have done

The cleaning compound was prepared by diluting 1 part cleanser with 14 parts water.

The cleanser is a common brand detergent (Sunlight Oxi Action, the grease fighter).

Cleaning

Standard requirement

a. The test panel shall be cleaned using a heavy duty wear tester, fitted with a cellulose sponge at speed setting of 5.
b. The sponge shall be cut such that the dimension parallel to the cleaning stroke is 3.5 inches and the width is 2.75 inches.
c. The cleaning head with the dry sponge attached shall be weighed to a mass of 600 ±10 grams.
d. After allowing a 30-second dwell time, the test panel shall be cleaned using 5 cycles of the wear tester, then turned 90 degrees and cleaned for an additional 5 cycles.

What we have done

The test panel was cleaned using a cellulose sponge, measuring 65 mm x 75 mm x 25 mm for the aluminium panels and 130 mm x 75 mm x 25 mm for the steel panels. A typical amount of diluted cleaner applied to the sponge for wetting is 40 ml for aluminium panels and 80 ml for aluminium panels. The total weight of the wet sponge and the load on top of it was kept at the same value, 300 g for the aluminium panels and 600g for the steel panels, to ensure each individual test panel under the same pressure. To avoid cross-contamination, a new sponge shall be used for each cleaning cycles. The panel was rinsed under cold running tap water and allowed to dry.

All the lightness values were measured using a colorimeter. The L_c value was measured at the end of the cleaning cycle when needed.

Evaluation

The percent cleaning efficiency for panel was determined as follows:

$$\text{Percent CE} = (Lc - Ls)/(Li - Ls)$$

Where: Percent CE = Cleaning efficiency
L_i = Initial Lightness
L_c = Cleaned Lightness
L_s = Soiled Lightness

Further testing

1. Hydrophobicity and oleophobicity tests

Hydrophobicity and oleophobicity tests were carried out by characterizing the contact angles, contact angle hysteresis and sliding angles, using both water and oil (mineral oil for sliding angle and hexadecane for contact angle).

2. Cleaning efficiency tests

The further testing was conducted in the same way as described above. The only difference is that the three coated samples were steel panels with larger size than the aluminium panels used in the initial testing. The sponge size and pressure on sponge were also changed accordingly.

2.2 Experimental Results

2.2.1 Initial testing

2.2.1.1 Selection of functional particles and the best loading ratio

Particle A, B and C were firstly treated to activate the particle surfaces and then incorporated into filler removed PSX-700 paint at four different dry-weight loading ratios ($W_{particles}$ / ($W_{dry\ resin}$+ $W_{particles}$), 10%, 15%, 20% and 25%. Aluminium panels coated with these modified paints were prepared for testing. The paints were applied on panels using a Mayer bar (RDS 26). Water and oil sliding angle testing, which is a quick and easy way to determine the water and oil repellence of a surface, were employed for the selection of functional particle type and the loading ratio. Results are shown in Table 1.

Particle C does not provide a high water and oil repellency and it significantly reduces the gloss of coating surface, although the surface smoothness was fairly good. It was noticed that Particle A makes the coating surface rough and dull and the sliding angles for both water and oil are high. This might be due to the relatively large particle size of Particle A which leads to a rough surface and impedes the free rolling of liquid droplet. Particle B provides the best water and oil repellence among the 3 types of functional particles. It was found that the coating surface with 15% of Particle B loading ratio shows the best water and oil repellence while the surface quality is acceptable. Therefore, a loading ratio of 15% Particle A was chosen for the successive experiments.

Table 1. Comparisons of the three types of functional particles

Functional Particle	Loading Ratio, %	Gloss	Smoothness 1 Low - 5 High	Average Water Sliding Angle, deg	Average Mineral Oil Sliding Angle, deg
A	10	79.1	4	23.5	18.3
	15	75.3	3	25.0	17.5
	20	75.2	2	26.0	18.7
	25	72.8	2	25.3	20.0
B	10	86.2	5	20.5	15.5
	15	83.4	5	21.3	15.5
	20	83.3	4	21.7	17.3
	25	82.9	4	21.0	17.0
C	10	74.7	5	22.0	16.5
	15	73.1	5	21.5	17.3
	20	73.0	5	23.0	19.7
	25	71.0	4	23.3	19.3

2.2.1.2 Adhesion testing

0.85 (lb-ft) of impact testing was employed to characterize the adhesion of the modified paints in comparison with the original PSX-700. As shown in Table 2, it was found that both the original paint and the modified paint failed with the impact testing, although the original paint has slightly better adhesion than the modified.

For the self-cleaning testing, coatings need to be characterized by the lightness change and therefore, the initial lightness of all coated panels should be made with as small a deviation as possible. Because the original PSX-700 is in military green and the modified paints are almost transparent, we decide to, for the successive experiments, prime the panels with the original PSX-700 before coating them with the modified paints. Therefore, a panel coated with PSX-700 as primer was tested for adhesion as well. It shows a similar adhesion as the one coated with only the original paint.

Table 2. Adhesion test results of the modified paint

Coating on Panel	Loading Ratio of Particle B, %	Average Film Thickness, µm	0.85 Lb-ft Impact Test
Panel Coated with Original PSX-700 (1 layer)	N/A	55	Fail (slightly better than the 1-layer modified paint)
Panel Coated with Paint Modified with Particle B (1 layer)	15	51	Fail
Panel Primed with Original PSX-700 and then Coated with Paint Modified with Particle B (1 layer original, 1 layer modified)	15	22 primer 35 modified paint	Fail (similar to the 1-layer original paint)

2.2.1.3 Cleaning efficiency testing

It was determined from the above tests that Particle B can be selected for further experiments and a loading ratio of 15% was chosen. Following the self-cleaning testing procedure altered from MIL-PRF-85570E, 3 control panels coated with original PSX-700 and 3 panels coated with modified paints were tested for self-cleaning efficiency. The 3 panels to be coated with the modified paint were firstly primed with the original paint before the modified paint was applied on.

Cleaning efficiency was measured after the first half cycle (1-Y, one wipe in Y direction in Cycle 1) and the second half cycle (1-X, one wipe in X direction in Cycle 1). And for the consequent cycles afterwards, the measurement was taken after Cycle 3 and 5. The results are shown in Table 3 and Figure 1. We found the resultant data did not demonstrate a very clear difference between the original paint (controls) and the modified paint. Instead, we could see a lot of contingency (occasionality). Even among the samples of the same paint, significant arbitrary deviations and inconsistencies existed. However, from the overall view of the cleaning processes, especially for the first cleaning cycle (1-Y plus 1-X), the samples coated with modified paint seemed to exhibit better self-cleaning efficiency. After Cycle 3, all samples became almost fully clean with very small differences. The performance of the modified paint will be further evaluated.

Table 3. Initial test results of self-cleaning efficiency

	Initial Lightness Li	Li Deviation	Soiled Lightness Ls	Ls Deviation	Cleaning Cycles	Cleaned Lightness Lc	Lc Deviation	Cleaning Efficiency CE
Control-1	48.69	0.078	23.25	0.638	1-Y	32.02	11.405	34.5%
					1-X	40.82	6.802	69.1%
					3	48.4	0.197	98.9%
					5	48.54	0.064	99.4%
Control-2	49.07	0.146	23.7	0.585	1-Y	38.43	6.39	58.1%
					1-X	47.6	0.946	94.2%
					3	49.12	0.066	100.2%
					5	49.17	0.28	100.4%
Control-3	49.19	0.219	22.64	0.445	1	47.31	1.262	92.9%
					2	49.14	0.076	99.8%
					3	49.12	0.122	99.8%
					5	49.05	0.139	99.5%
M-1	51.01	0.309	22.98	0.192	1-Y	42.99	4.099	71.4%
					1-X	50.44	0.293	98.0%
					3	50.63	0.393	98.6%
					5	50.89	0.018	99.6%
M-2	50.87	0.369	23.13	0.235	1-Y	49.97	0.407	96.8%
					1-X	50.7	0.355	99.4%
					3	50.84	0.255	99.9%
					5	50.86	0.016	100.0%
M-3	51.65	0.213	22.97	0.402	1-Y	38.12	9.903	52.8%
					1-X	42.88	9.739	69.4%
					3	50.97	1.296	97.6%
					5	51.76	0.561	100.4%

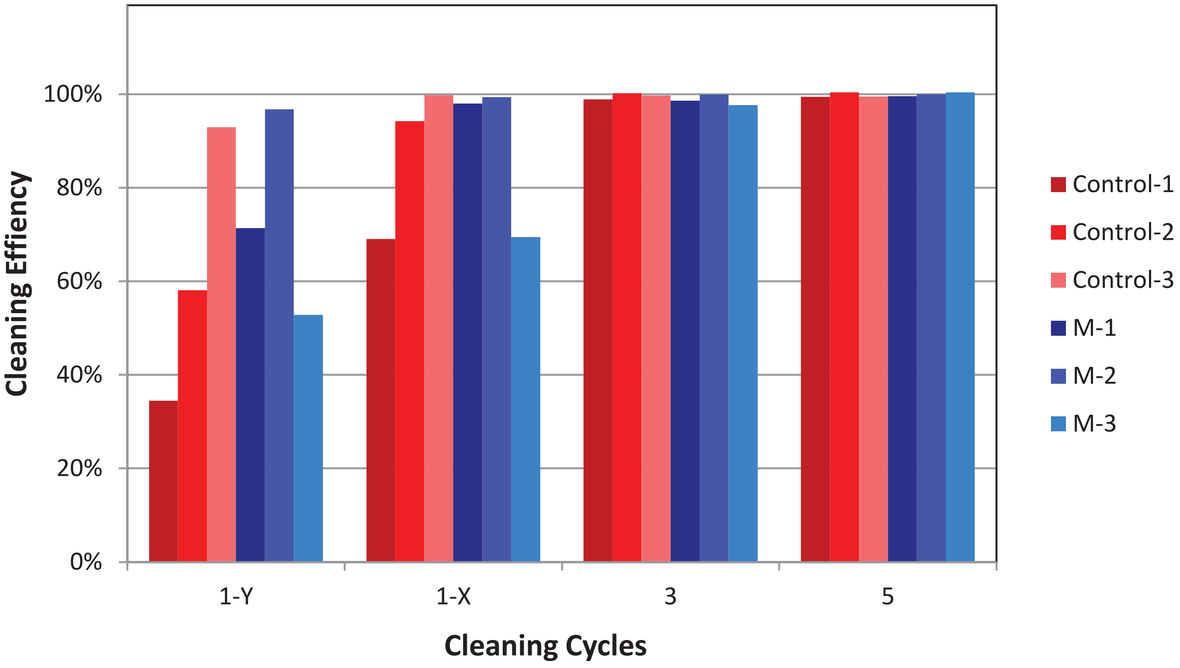

Figure 1. Initial test results of self-cleaning efficiency

Figure 2 shows the pictures of these panels when half cycle and full cycle of Cycle 1 was done as well as when Cycle 5 was done. It was noticeable that because of the recessed strips on the coating surfaces (which were the coating-tool marks caused by the wires on the Mayer bar), soil could hide in these strips of recessed areas. To eliminate the influence of the coating tool marks, the steel panels were coated for the further testing using a sprayer, although the film thickness control with a sprayer was more difficult.

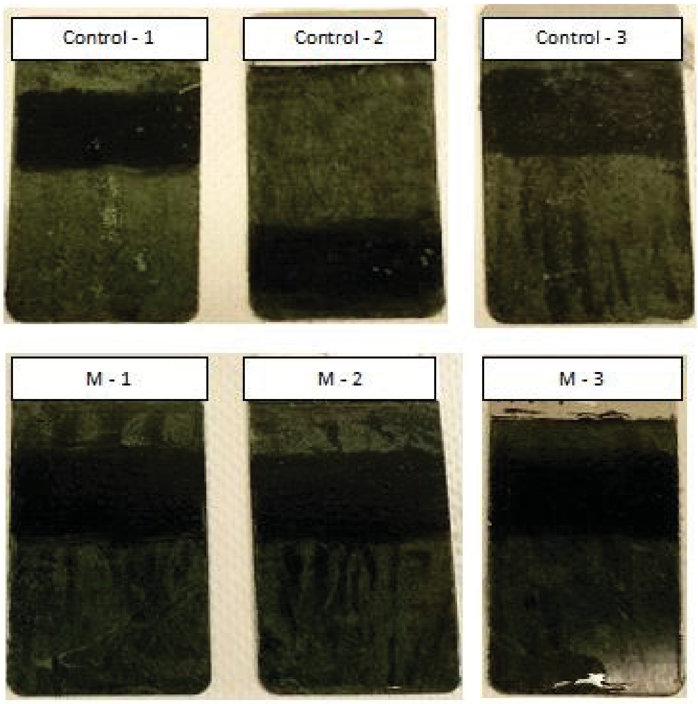

Figure 2a. Soiled panels

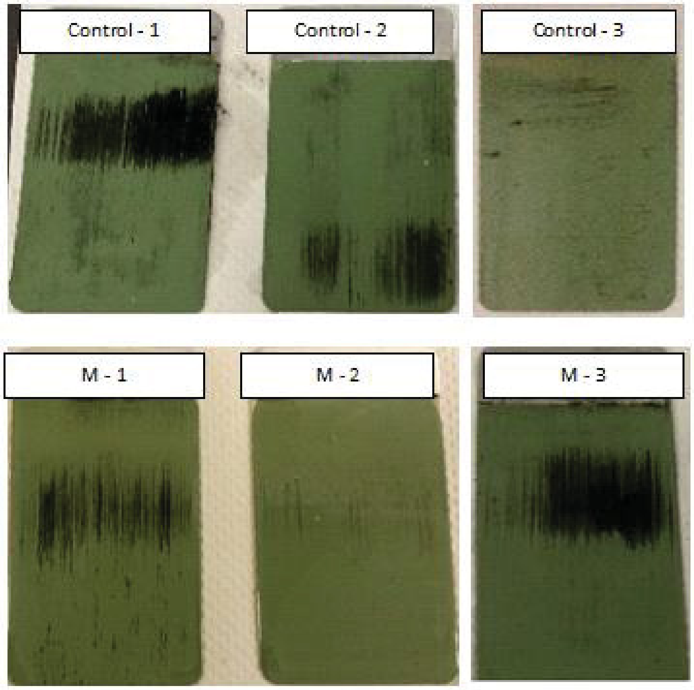

Figure 2b. After 1-Y of Cycle 1

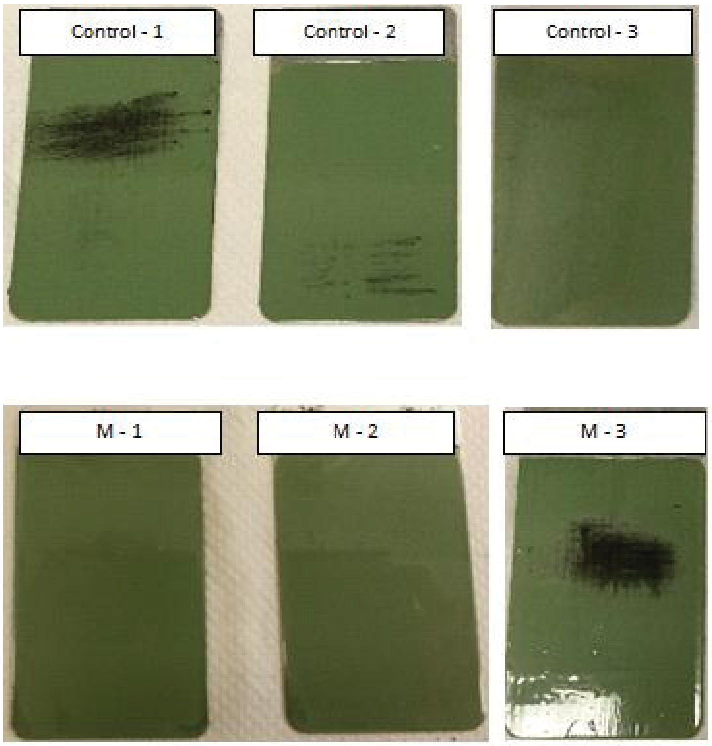

Figure 2c. After 1-X of Cycle 1

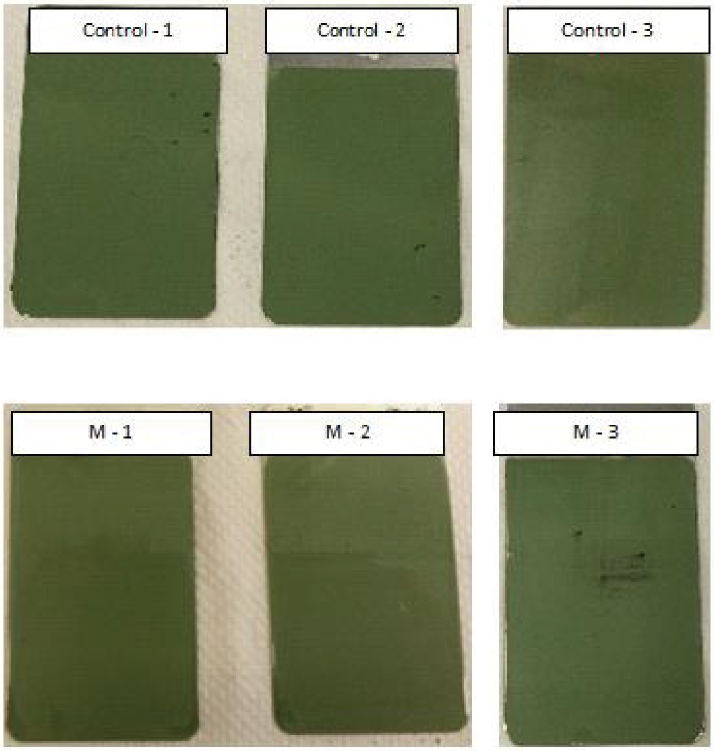

Figure 2d. After Cycle 5

2.2.2 Further testing

Based on the results from the initial testing, three more coated panels were prepared for the further testing. The substrates were 3 x 6 inch steel panels. The three sample panels for further testing were: Control-4 coated with original PSX-700 (1 layer, 69 µm film thickness), Control-5 coated with filler-removed PSX-700 (with original PSX-700 as primer, 58 µm total film thickness) and M-4 coated with modified paint (with original PSX-700 as primer, 78 µm total film thickness). Of course, for the top layer of sample M-4, 15% loading ratio of Particle B was used. To avoid the coating-tool marks on the film surfaces, these panels were coated with a sprayer instead of Mayer bar.

2.2.2.1 Hydrophobicity and oleophobicity tests

Hydrophobicity and oleophobicity tests were carried out by characterizing the contact angles, contact angle hysteresis and sliding angles, using both water and oil (mineral oil for sliding angle and hexadecane for contact angle).

Test results are listed in Table 4. From Table 4a, we can see that the modified paint (M-4) has similar hydrophobicity, represented by the sliding angle, contact angle and contact angle hysteresis, as the original paint (Control-4, PSX-700). This means that the modification of the paint retained the hydrophobicity, if not increased it. By comparing the modified paint with the filler-removed PSX-700 (Control-5), it is seen that the addition of functional particles increased the contact angle but also increased the contact angle hysteresis. Therefore, the sliding angle remained unchanged.

Table 4a. Hydrophobicity test results in further testing

Sample	Ave Water Sliding Angle, deg	Ave Water Contact Angle, deg	Ave Water Advancing Angle, deg	Ave Water Receding Angle, deg	Ave Water Contact Angle Hysteresis, deg
Control-4	21.2	80.8	89.3	55.8	33.5
Control-5	21.3	77.8	83.0	52.5	30.5
M-4	21.5	80.8	87.1	53.5	33.6

As shown in Table 4b, the modified paint (M-4) exhibited higher oleophobicity, represented by the lower sliding angle and smaller contact angle hysteresis, than the original paint (Control-4, PSX-700). Comparing with the filler-removed PSX-700 (Control-5), the modified paint showed higher oil repellence, implying that the addition of functional particles increased the oleophobicity of the resin system. On the other hand, when comparing the original paint to the filler-removed, the former had a lower oleophobicity, suggesting that the filler employed in the original paint may have a negative effect on the oleophobicity.

Table 4b. Oleophobicity test results in further testing

Sample	Ave Mineral Oil Sliding Angle, deg	Ave Hexadecane Oil Contact Angle, deg	Ave Hexadecane Advancing Angle, deg	Ave Hexadecane Receding Angle, deg	Ave Hexadecane Contact Angle Hysteresis, deg
Control-4	17.3	8.3	13.7	6.3	7.3
Control-5	15.0	10.3	13.7	7.7	6.0
M-4	14.5	7.3	12.0	6.3	5.7

2.2.2.2 Cleaning efficiency tests

Cleaning efficiency tests in the further testing was conducted in the same way as that in the initial testing. The only difference is that the three coated samples were steel panels with larger size than the aluminium panels used in the initial testing. The sponge size and pressure on sponge were also changed accordingly. Test results are given in Table 5, Figure 3 and Figure 4.

The results showed that all three samples cleaned up fairly quickly. After the completion of the first wiping cycle, they became almost fully clean. The results seem to confirm that the modified paint had a higher self-cleaning efficiency, although as mentioned before, more reliable evaluations still need to be performed.

Table 5. Further test results of self-cleaning efficiency

	Initial Lightness Li	Li Deviation	Soiled Lightness Ls	Ls Deviation	Cleaning Cycles	Cleaned Lightness Lc	Lc Deviation	Cleaning Efficiency CE
Control -4	49.19	0.219	22.8	0.318	1-Y	44.86	2.022	83.6%
					1-X	48.80	0.325	98.5%
					2	49.05	0.181	99.5%
					3	49.05	0.183	99.5%
Control -5	50.01	0.16	22.94	0.363	1-Y	41.73	5.362	69.4%
					1-X	49.72	0.165	98.9%
					2	49.76	0.098	99.1%
					3	49.89	0.167	99.6%
M-4	51.83	0.292	22.4	0.502	1-Y	51.27	0.163	98.1%
					1-X	51.51	0.353	98.9%
					2	51.58	0.324	99.2%
					3	51.55	0.236	99.1%

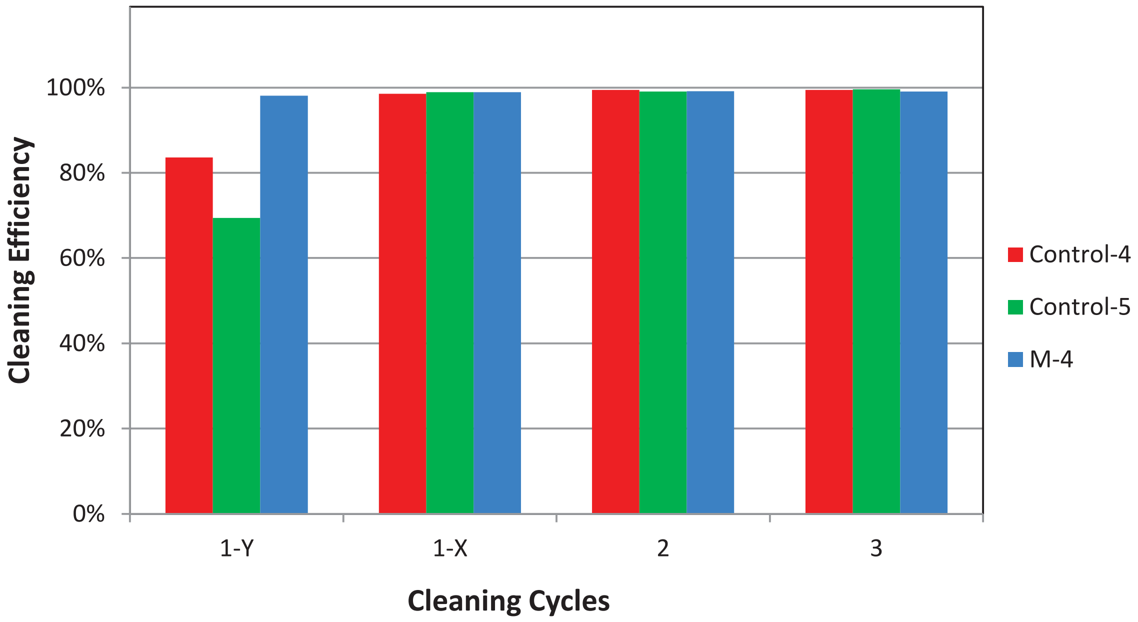

Figure 3. Further test results of self-cleaning efficiency

Figure 4a. After 1-Y of Cycle 1

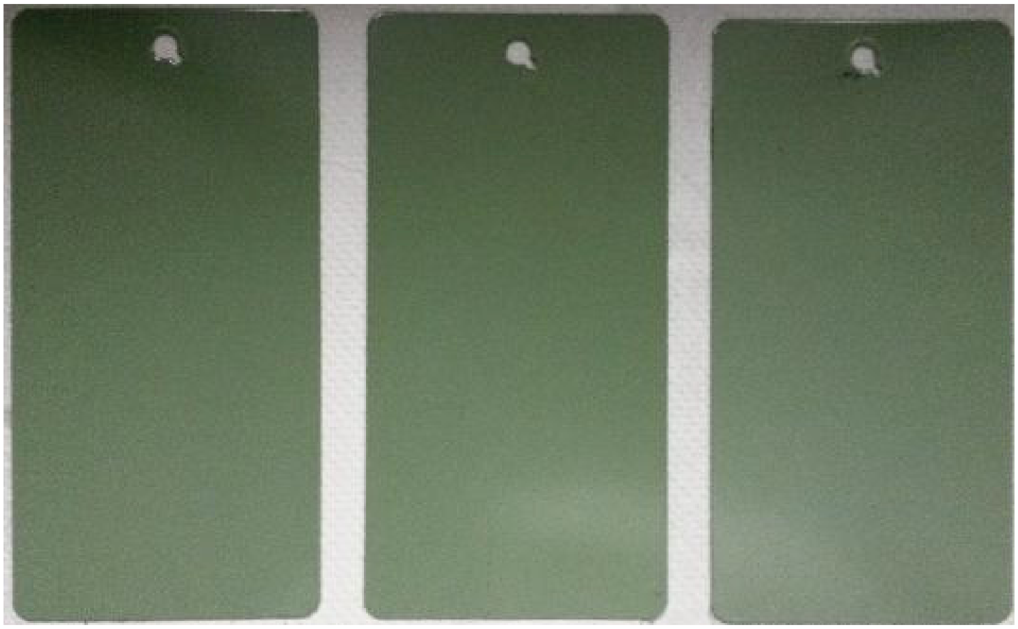

Figure 4b. After 1-X of Cycle 1

3. Discussions and conclusions

Three different types of functional particles were tested and a formulation and process was developed for producing a durable self-cleaning military coating. Sample paints using a modified polysiloxane, PSX-700, were evaluated in regards to their hydrophobicity, oleophobicity and self-cleaning efficiency.

Screening of three types of functional particles, which are either pure fluorinated polymer or compound of fluorinated polymer and polypropylene, possessing certain degrees of hydrophobicity and oleophobicity, was conducted by comparing the functionality of the modified coatings. The optimum concentration of the functional particles was determined by evaluating their water and oil repellency performance. In order to make the functional particles used in this research dispersible in the resin-solvent system of the paint, a plasma particle surface treatment was employed to activate the surfaces of the functional particles. This treatment also makes the particles bond better to the resin system of the paint.

The modified paint from this research has similar hydrophobicity to the original paint, PSX-700. However, it demonstrates higher oleophobicity than the original paint and this property is important for the target function: self-cleaning effect to both water and oil borne contaminations.

Self-cleaning efficiency tests were performed using a procedure that mainly follows the MIL-PRF-85570E standard but with some alternative steps adopted. It was found that the resultant data did not demonstrate a very clear difference between the original paint (controls) and the modified paint. However, from the overall view of the data obtained the modified paint seemed to exhibit better self-cleaning efficiency. Further testing is required.

This research was a provisional and start-up work in fabricating amphiphobic coatings that facilitate the removal of both water and oil borne contaminations, by incorporating functional particles into the paint system. There are yet many other factors and parameters to be looked into to optimize the final results. Conditions of the special treatment for particle surface activation, broader types of functional particles, more precise selection of particle concentrations and improvement of particle incorporation processes are all pending for further investigations if such a promising approach used in this research is to be brought into a real application.

4. Outlook of future work

Improvement in oleophobicity of a military coating has been achieved in this research. Possible enhancement of self-cleaning efficiency of the modified paint is to be confirmed by facilities capable of performing the standard testing.

Fabrication of amphiphobic coatings is still a new area for investigation. This research explored a new approach, in which functional amphiphobic particles were pre-treated and incorporated into the paint, to obtain the self-cleaning effect. However, this was a provisional and exploratory work, given the fact that almost no relevant reports could be retrieved and no real commercial products were available.

Based upon the encouraging results from this research, fabrication of amphiphobic coatings that facilitate the removal of both water and oil borne contaminations is possible by this approach, i.e. incorporating functional particles into the paint system. To bring such a promising approach into authentic applications, many other factors and parameters pending for study are to be looked into to optimize the final results. Involved in these to-be-studied, conditions of the plasma treatment for particle surface activation, broader types of functional particles, more precise selection of particle concentrations and improvement of particle incorporation processes are yet subject to further investigations.

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