Final Technical Report

Project Title:	[Development of Low Fouling/High Fouling-release and Self-polishing Nonfouling Marine Coatings]
Period Covered by the Report:	[Aug. 18, 2016 to Jun. 30, 2018]
Security classification:	[unclassified]
Name of the activity issuing the award document:	US Navy / Office of Naval Research

ONR Grant

Contract Number:	[N00014-16-1-2987]
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Program Objective

This grant from ONR to NatureCoat LLC is to develop, scale up/formulate and study 1) low fouling/high fouling-release marine coatings and 2) self-polishing nonfouling marine coatings. The success of this work will facilitate the efforts to develop next-generation marine coatings exceeding the performance of existing commercial coatings. It serves to meet the long-term goal of the ONR coatings program for the development of environmentally benign, effective and long-lasting marine coatings.

Work progress and significant events by task

1) Low fouling/high fouling-release marine coating

1. Synthesis of zwitterionic compound

For this project, zwitterionic compound and PDMS material are integrated together to achieve low fouling/high fouling-release marine coatings. Following the pre-established procedure, the production of zwitterionic compounds with different structures were achieved. During this project, the production capability was increased so that 1 gallon of designed marine coating can be readily prepared.

2. Coating preparation and sagging test

Previous effort has been taken to integrate zwitterionic compound and PDMS material together along with various additives into applicable marine coatings. The typical procedure is that PDMS containing zwitterion (Part A) are mixed with cross-linker and catalyst (part B) to form coating a mixture. The mixture is stirred vigorously until all the solid is dispersed uniformly. The obtained viscous coating is then applied onto aluminum panels. The coating cures within 3 hours. These coatings are inspected for any cracks on the surface. With the support of this grant, we are able to test further several coating parameters, including zwitterionic compound type, zwitterion content, cross-linker amount, catalyst amount, pigment amount and thixotropy amount. Following the same procedure, by verifying those parameters, different formulations were designed and applied onto aluminum panels for field test. Sag test of marine coating is important for applying paints onto vertical surfaces. To ensure success of boat tests, sag behavior needs to be adjusted. To obtain appropriate sagging behavior, a different amount of thixotropy was added into the coating mixture to adjust viscosity. Sag behavior was observed and subsequently adjusted by changing thixotropy amount. **Figure 1** below shows marine coating with different sagging behaviors.

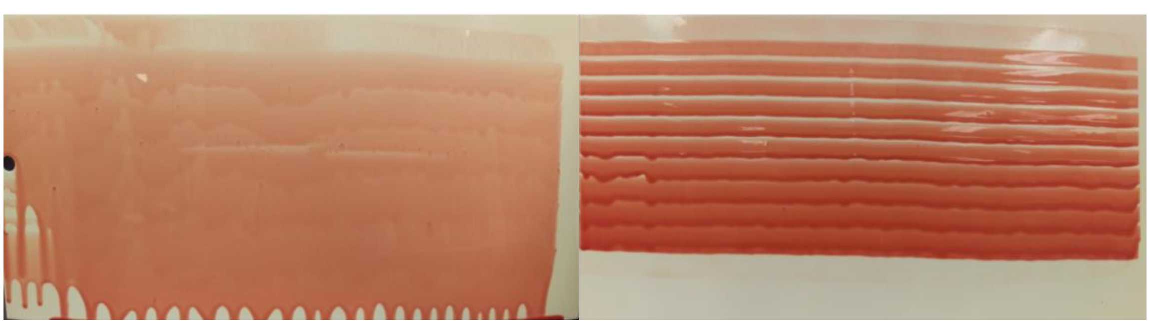

Figure 1. Sag behaviors of coating formulations applied on an anti-sag meter. 1) Coating with server sag (left); 2) Coating with appropriate sag (right).

3. Preparation of testing panels

The coating formulation has been developed and optimized, particularly in term of physical properties. The designed formulations are applied onto aluminum panels of 4 inch × 8 inch using brush, roller or spray (industrially preferred). All coatings are durable and adhered onto substrates strongly. To evaluate our coating performance, they were sent to Florida Institute of Technology (FIT), Singapore and Hawaii testing sites (3 panels for each site). These formulations were tested in 3 batches at 3 different time points. They are summarized below.

Table 1. Coating formulation codes.

1st batch (March, 2017)		**2nd batch (September, 2017)**	
N-X-1	Zwitter 1; low; Brush	N-X-7	Zwitter 4; medium; Spray
N-X-2	Zwitter 1; low; Spray	N-X-8	Zwitter 4; high; Spray
N-X-3	Zwitter 2; low; Brush	N-X-9	Zwitter 5; medium; Spray
N-X-4	Zwitter 2; low; Spray	N-X-10	Zwitter 5; high; Spray
N-X-5	Zwitter 3; low; Brush	N-X-11	Zwitter 4; high; Brush
N-X-6	Zwitter 2 + CPT; low; Brush	N-X-12	Zwitter 4; high; Air Spray
Low – Low zwitter content Medium – Medium zwitter content High – High zwitter content		- Low VOC to match commercial coatings - Coating applied vertically	
3rd batch (April, 2018)			
N-X-13	Zwitter 6; low; Spray	N-X-18	Zwitter 7+ Zwitter 11; Medium; Spray
N-X-14	Zwitter 7; low; Spray	N-X-19	Zwitter 6 ; High; Spray
N-X-15	Zwitter 8; low; Spray	N-X-20	Commercial hydrophobic compound; Spray
N-X-16	Zwitter 9; low; Spray	N-X-21	Zwitter 7 + additional solvent; Low; Spray
N-X-17	Zwitter 10; low; Spray		
-Test more zwitterionic compounds.			

4. Field Test Results and Discussion.

1. Field test results for 1st batch (immersed in seawater in March, 2017)

The images of testing panels in Singapore for the 1st batch are shown in **Figure 2**. Those panels were immersed in Singapore testing site for 12 months. The top half of coatings were remained no touch (testing nonfouling performance), while the bottom half of coatings were cleaned by water jet (testing fouling-release performance). From those images, compared to IS970 commercial reference, the N-X-4 formulation is obviously the best performer in the 1st batch which was made with zwitterionic compound (zwitter 2).

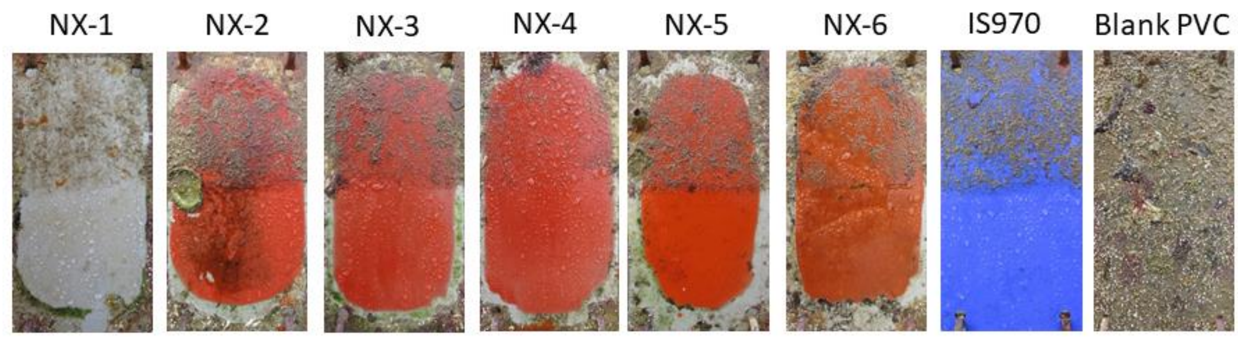

Figure 2. Coating images from Singapore (1st Batch, 12-month immersion).

The anti-fouling results from FIT shown in **Figure 3** (left) indicated that the formulation N-X-4 has significantly lower initial fouling (less than 50%) than IS970 reference, while the "fouling-release" performance of this batch shown in **Figure 3** (right) are all better than IS970. The overall best performer is still the formulation N-X-4.

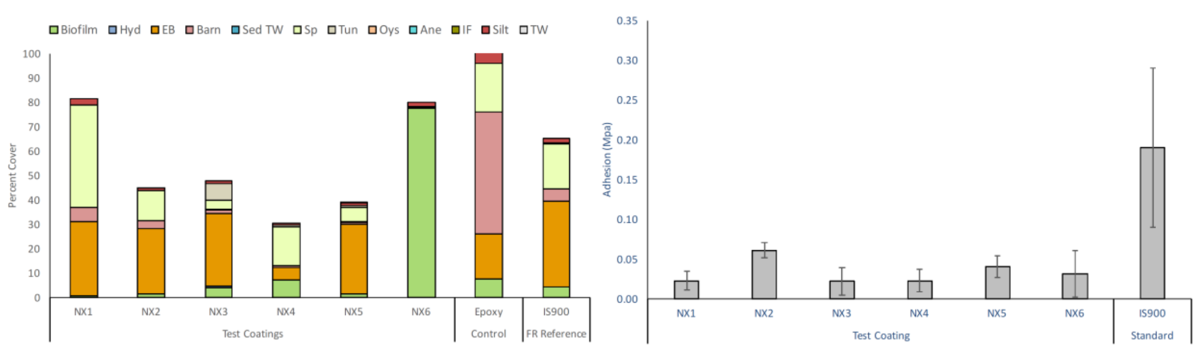

Figure 3. Average percent cover of fouling organism observed after 5-month immersion (Left) and tubeworm adhesion (Data from FIT).

Moreover, the images for the first batch coatings which were immersed in Hawaii testing site for 386 days are shown in **Figure 4**, in which N-X-4 has the least foulants attached on the surface.

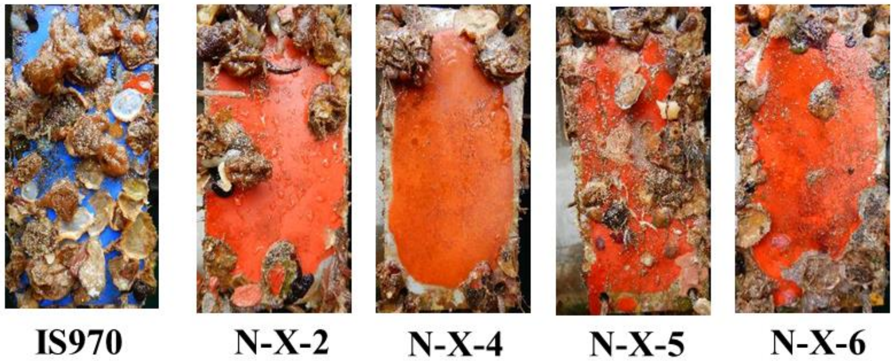

Figure 4. NatureCoat Coating Images after 386-day immersion in Hawaii.

In summary, for the first batch, the results from all three testing sites are consistent which all demonstrate that N-X-4 is the top performer in term of low initial fouling and high "fouling-release".

2. Field test results for 2^nd batch (immersed in seawater in September, 2017)

As concluded above, the N-X-4 (zwitter 2) is the best formulation in the first batch. To repeat this result, the second batch was prepared by slightly varying zwitterionic compound structure and content (see Table 1). The field test results for the second batch from FIT are shown in **Figure 5**. The coating images indicate that NatureCoat N-X-10 has better nonfouling (Left) performance than IS970 control (Middle). Furthermore, as shown in **Figure 6**, all 6 formulations have lower percent coverage than IS970. Among them, the fouling organisms attached on 4 formulations (N-X-9, N-X-10, N-X-11 and N-X-12) surfaces are less than 20% of those on IS970.

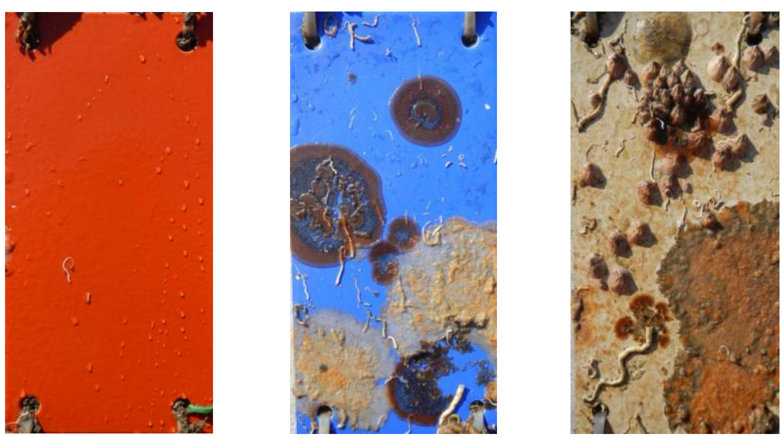

Figure 5. Coating images from FIT, NatureCoat N-X-10 (left), IS 970 (middle) and epoxy (right) (2nd Batch, 225-day immersion).

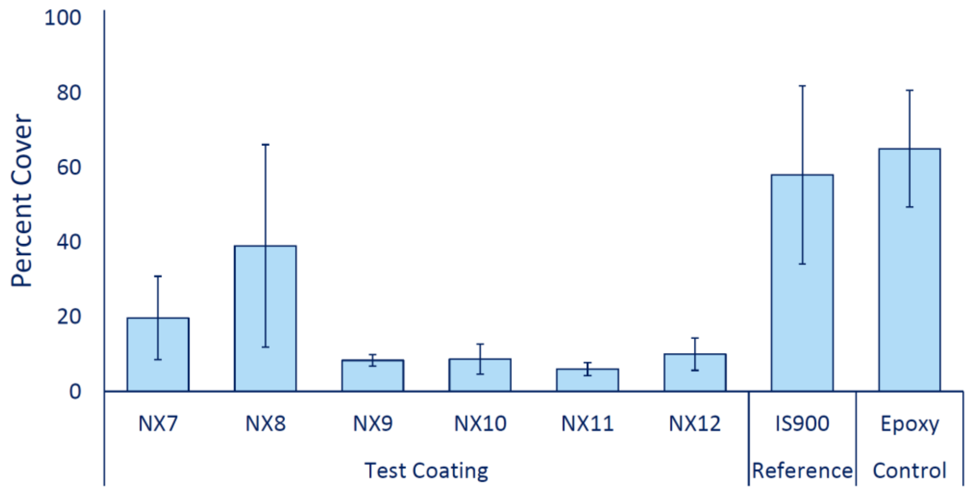

Figure 6. Average percent cover of fouling organism observed after 256-days immersion (Data from FIT).

Thus, these results further repeated the good performance of N-X-4. It demonstrated that zwitter 2 is the best compound for low fouling and high "fouling-release" marine coating.

3. Field test results for 3rd batch (immersed in seawater in April, 2018)

To further explore more parameters, more zwitterionic compounds were produced using a simplified synthetic strategy with fast reaction and no purification, leading to quicker and lower cost for zwitter production. Moreover, the simplified method is easier to scale up. These compounds were integrated with PDMS material following the same protocols used for preparing the first and the second batches.

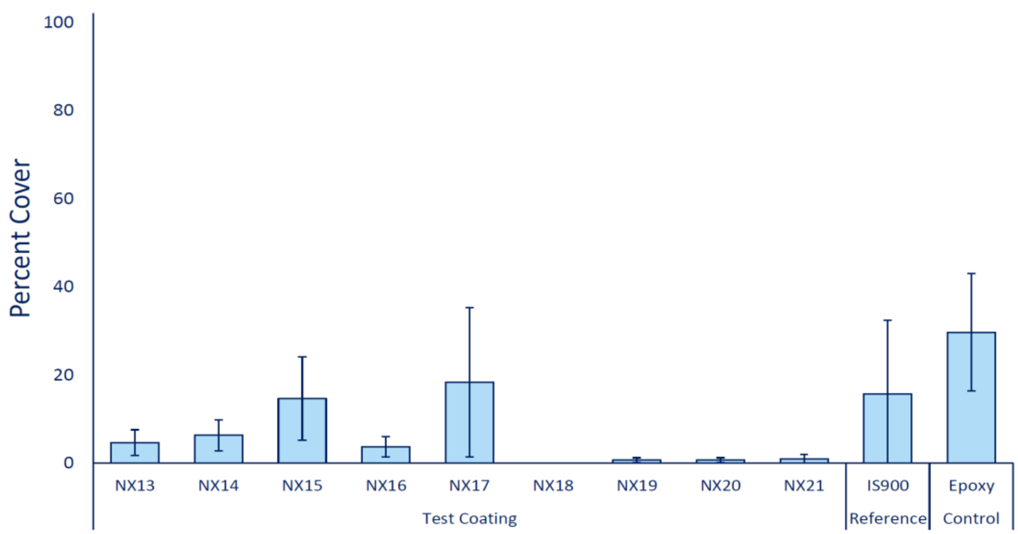

Figure 7. Average percent cover of fouling organism observed after 1 month immersion (Data from FIT).

The field test results for the 3rd batch are shown in **Figure 7**, in which 7 out of 9 formulations have less initial fouling percent cover than commercial IS970 reference. Among them, fouling organisms attached on N-X-18, N-X-19, N-X-20 and N-X-21 are significantly low. The results are promising and encouraging.

6. Conclusions:

In conclusion, extensive work has been carried out to develop, scale up/formulate and study the production of zwitterionic compounds. The production capability is increased by 10 times during this project. The zwitterionic compound number 2 (zwitter 2) is demonstrated to be the best compound to achieve low fouling and high “fouling-release” marine coatings. Several marine coatings made from new zwitterionic compounds which are synthesized by a simplified strategy have significantly low initial fouling. Those formulations are still under long-term field tests.

2) Self-polishing nonfouling marine coating

While low fouling and high-fouling released is the main focus of this project, we have also worked on self-polishing nonfouling marine coatings. For zwitterionic (Q) formulation, degradable zwitterionic precursor is hydrolyzed to zwitterion to provide nonfouling effect upon its contact with seawater. The coating formulation has been adjusted and applied onto fiberglass panels of 4 inch × 8 inch using brush method. To evaluate our coating performance, they were sent to FIT and Singapore testing sites (3 panels for each site). These formulations were tested in 5 batches at 5 different time points. A comparison of all formulations is listed in Table 2.

Table 2. Coating formulation codes.

1st batch (Feb, 2017)		**2nd batch (Apr, 2017)**	
Q-1	Low Q; medium HD; high HO	Q-8	Medium Q; low HD; medium HO
Q-2	Low Q; medium HD; high HO; low CL	Q-9	Medium Q; low HD; medium HO; low CL
Q-3	Medium Q; low HD; high HO	Q-10	Medium Q; medium HD; medium HO
Q-4	Medium Q; low HD; high HO; low CL	Q-11	Medium Q; medium HD; medium HO; low CL
Q-5	Medium Q; medium HD; high HO	Control	BRA640
Q-6	Medium Q; medium HD; high HO; low CL		
Q-7	Medium Q; medium HD; high HO; low Cu_2O		
Control	BRA640		
Low Q– Low zwitterionic content Medium HD– Medium hard content Medium HO– Medium hydrophobic content Low CL – Low crosslinker content		Test more zwitterionic compounds.	

3rd batch (Aug, 2017)		**4th batch (Dec, 2017)**		**5th batch (Apr, 2018)**	
Q-12	Medium Q; high HD; medium HO; low CL	Q-16	Low Q; low HD; medium HI; medium CL	Q-20	Low Q; low HD; high HI; medium CL
Q-13	Medium Q; high HD; medium HO; medium CL	Q-17	Low Q; low HD; medium HI; high CL	Q-21	Low Q; low HD; high HI; high CL
Q-14	Low Q; low HD; high HI; low CL	Q-18	Low Q; low HD; high HI; medium CL	Control	BRA640
Q-15	Low Q; low HD; high HI; medium CL	Q-19	Low Q; low HD; high HI; high CL		
Control	BRA640	Control	BRA640		
HI – Hydrophilic content Adjust hydrophilic and crosslinker compounds.		Adjust hydrophilic compounds.		Test more zwitterionic compounds and adjust hydrophilic compounds.	

There are more than 100 panels have been sent out for field test so far. Several parameters such as nonfouling content (Q), hydrophobic to hydrophilic ratio, hard and soft components, hydrophilic compounds and crosslinker amount were investigated. Coating stability, nonfouling and self-polishing rate were measured and adjusted for better performance.

Ongoing work

After extensive investigation of all parameters related to stability, nonfouling and self-polishing, the performance of these coated panels has been improved in all of these three aspects. In order to ensure long-term stable hydrolysis rate and excellent nonfouling behavior, we have designed another self-polishing zwitterionic precursor. As shown in **Figure 8**, coatings containing a different amount of the 2nd generation zwitterionic components have been tested in artificial seawater. The results show that all tested coatings stay transparent after immersion for 45 days. The new hydrolyzed product dissolves in seawater easily, providing a good self-polishing behavior and maintaining the transparency of the coating. Several formulations made from the 2nd generation of the 2nd generation zwitterionic compounds are being screened before the next field test.

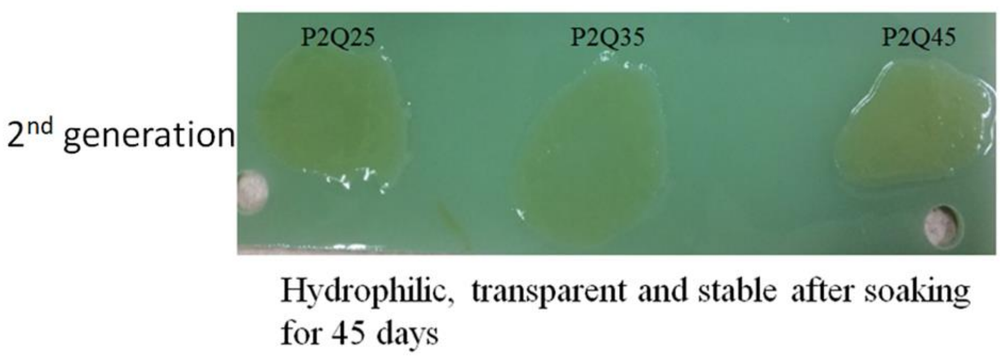

Figure 8. A new 2nd generation zwitterionic compound is designed for long-term stable hydrolysis rate and excellent nonfouling behavior.

Identification of any technical and/or programmatic issues

No issues; the project is going on well as planned.

Transition progress or updates to plan

No update to the plan.

REPORT DOCUMENTATION PAGE	*Form Approved* *OMB No. 0704-0188*

1. REPORT DATE *(DD-MM-YYYY)*	**2. REPORT TYPE**	**3. DATES COVERED** *(From - To)*
23-08-2018	Final Technical Report	Aug 2016 - Jun 2018

4. TITLE AND SUBTITLE Development of Low Fouling/High Fouling-release and Self-polishing Nonfouling Marine Coatings	**5a. CONTRACT NUMBER** N00014-16-1-2987
	5b. GRANT NUMBER N00014-16-1-2987
	5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S) Xuewei Xu	**5d. PROJECT NUMBER**
	5e. TASK NUMBER
	5f. WORK UNIT NUMBER
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) NATURECOAT LLC 14507 NE 61ST ST REDMOND WA 98052-4680 UNITED STATES OF AMERICA	**8. PERFORMING ORGANIZATION REPORT NUMBER**
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Office of Naval Research 875 N. Randolph Street Suite 1425 Arlington VA 22203-1995	**10. SPONSOR/MONITOR'S ACRONYM(S)**
	11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for Public Release; Distribution is Unlimited

13. SUPPLEMENTARY NOTES

14. ABSTRACT
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15. SUBJECT TERMS
Nonfouling and high fouling-release marine coating; environmental benign

16. SECURITY CLASSIFICATION OF:			**17. LIMITATION OF ABSTRACT**	**18. NUMBER OF PAGES**	**19a. NAME OF RESPONSIBLE PERSON**
a. REPORT	**b. ABSTRACT**	**c. THIS PAGE**			**19b. TELEPHONE NUMBER** *(Include area code)*
U	U	U	UU	9	703-696-5031