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REPORT NUMBER ONRC4
Final Report

ANTI-ICING CHITIN COATING SYSTEM DEVELOPMENT

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Authors--Fourth Report

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Performing Organization

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410 Chipeta Way, Suite 222
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Sponsoring Organization

Office of Naval Research
800 North Quincy Street
Arlington, Virginia 22217-5000

Project Scientist

Captain Steve Snyder

Abstract

Three concerns face marine paint manufacturers: anti-icing and antifouling capability and environmentally safe waste disposal. First, icephobic paints must prevent ice formation which leads to drag and structural damage. Conventional ship bottom coatings are based on 1) asphalt/oil media pigmented with a lead sulfate/aluminum and 2) a tung oil/phenolic medium. Second, antifouling paints must inhibit barnacles, algae and fungi destruction. Current paints contain TBT, cuprous oxide, mercury, water-soluble acrylic organotin polymer or polysiloxane silicone. Federal regulations require replacement of the coatings and antifouling materials in the next few years. Last, all liquid-applied spray coatings are subject to transfer efficiency of less than 50%. The overspray clogs grates, interferes with spray booth airflows, and must be separated and disposed. Usually, the sludge is landfilled, producing downstream pollution. Technical Research Associates has verified the icephobic and antifouling potential of blended chitin/ and chitosan/paints. Experiments have also established the feasibility of chitin/paint mix biodegradation.

Identifiers/Open-Ended Terms

Chitin
Chitosan
Icephobic Paint
Antifouling Paint
Enzymatic Degradation of Paint

Availability

Defense Technical Information Center
Bldg. 5, Cameron Station
Alexandria, Virginia 22314

Security Class

Unclassified
Unlimited

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Technical Research Associates would like to thank Captain Steve Snyder, Office of Naval Research, Arlington, Virginia, Project Scientist, for his support of the work. TRA would also like to acknowledge Ms. Russelle Dunson, ONR Contract Officer, for her assistance. The time and effort they have put into the project is greatly appreciated.

FORWARD

This Technical Report covers work performed on Contract NOOO14-90-C-0062, entitled " ANTI-ICING CHITIN COATING SYSTEM DEVELOPMENT", technically from September 1, 1990 through October 30, 1990. This program was sponsored by the Office of Naval Research, 800 North Quincy Street, BCT #1, Arlington, Virginia 22217-5000. The Project Scientist was Captain Steve Snyder.

Mrs. Gail Bowers-Irons was both the Project Manager and Principal Investigator. Mrs. Bowers-Irons and Ms. Amy Lai were responsible for this quarter's experimentation.

SUMMARY

Technical Objective:

The objectives of this project were to develop a standard icephobic chitin/chitosan paint system that could be easily and inexpensively produced and employed; to determine if the chitin/chitosan paint mix was effectively antifouling and to determine if the chitin/chitosan paint mix could be efficiently biostripped via chitinase reaction.

Work Statement:

The project was divided into five tasks. Task I focused on the development of homogenous chitin or chitosan suspensions. Once the chitin and chitosan addition techniques were optimized, Task II work determined the chitin/chitosan-paint suspensions standard ASTM test characteristics. Tasks III, IV and V centered on the icephobic, antifouling and biostripping investigations.

Approach:

The work in this project first focused on the production of homogenous chitin or chitosan suspensions. These suspensions were then added to Mil Spec polyurethane or epoxy paints in order to provide icephobic, antifouling and biodegradable coatings. ASTM coating tests were run to determine stability and consistency.

Fourth Report Work:

In this anti-icing chitin coating system development,
Technical Research Associates:

- o Verified the icephobic and antifouling potential of mechanically blended chitin/ and chitosan/paints.
- o Verified the icephobic and antifouling potential of chemically blended chitin/paints.
- o Established the feasibility of chitin/paint mix biodegradation.

INTRODUCTION

"Marine coatings represent a \$1 billion specialty segment of the world paint market. Paint supplied to this market must survive under the harshest environmental conditions and so suppliers must formulate the most durable coatings available. Recently, these high-value-added paints have come under many of the same pressures that have forced other industrial paint makers to reformulate paints." (1)

Three concerns face marine paint manufacturers: anti-icing and antifouling capability and environmentally safe waste disposal. First, icephobic paints must prevent ice formation which leads to drag and structural damage. Conventional ship bottom coatings are based on 1) asphalt/oil media pigmented with a lead sulfate/aluminum and 2) a tung oil/phenolic medium. Federal regulations require replacement of these materials in the next few years. To date, replacements have not become commercially available.

Second, antifouling paints must inhibit barnacles, algae and fungi destruction. Courtauld's tributyl tin (TBT) copolymer (*Intersmooth SPC*) erodes slowly but requires expensive hull preparation. Courtauld, Jotun, Kansai Paint and Chugoku Marine Paint manufacturer TBT-free ablative paints. These paints, however, contain cuprous oxide, mercury, water-soluble acrylic organotin polymer or polysiloxane silicone. The EPA, in July, banned the use of mercury. Methyl chloroform--1,1,1-trichloroethane, cuprous oxide and organotin polymers are due for phase out. (1) Manufacturers of marine paint must therefore replace current antifouling compounds.

Last, all liquid-applied spray coatings are subject to transfer efficiency of less than 50%. The overspray clogs grates, interferes with spray booth airflows, and must be separated and disposed. According to Ed Kliff, vice president of chemical industry consultants Phillip Townsend Associates, the current paint overspray market is about \$50 million. This waste can be used in cement kiln operations as filler and fuel supplement or in secondary paint manufacture. Usually, the sludge is landfilled, producing downstream pollution. (1)

In this anti-icing chitin coating system development, Technical Research Associates:

- o Verified the icephobic and antifouling potential of mechanically blended chitin/ and chitosan/paints.
- o Verified the icephobic and antifouling potential of chemically blended chitin/paints.
- o Determined the feasibility of chitin/paint mix biodegradation.

PROCEDURES

Materials

In addition to the materials used in report ONRC1 (4/30/90), ONRC2 (6/30/90) and ONRC3 (8/30/90), the following materials have been tested:

Methanesulfonic Acid--99%
Aldrich Chemical Company.
M860-6. Lot #:09307HX.

p-toluoyl Chloride--98%
Aldrich Chemical Company.
10,663-1. Lot #: 01425JW.

Ether--absolute, ACS reagent.
Aldrich Chemical Company.
34,613-6. Lot #: 00117CW.

A complete list of supplies is shown in the Appendix.

Fourth Phase Experimental

Following work by Blake, D. and Somorin, O., Nishi, N., Tokura, S. and Junzo, N. (1979), TRA workers prepared an organic-solvent soluble chitin. This benzoylated chitin derivative {p-methylbenzoyl chitin (PMBC)} was found soluble in butanol, dimethyl sulfoxide (DMSO), dimethyl formamide (DMF) and DESOTO mil T-81772A thinner.

To prepare the PMBC, several approaches were taken. In the first, 1 gm of Sigma C-4666 chitin was added to a 0°C-250 ml dry beaker in an ice bath. A very viscous gel formed on addition of 7 ml methanesulfonic acid. Next, 3.8 ml p-toluoyl chloride was added dropwise. Constant mixing was required but proved difficult. After several attempts, this first method was discarded.

In a modified second approach, the 7 ml of methanesulfonic acid was placed in an empty, dry, 0°C-250 ml beaker. 1 gm of Sigma-C-4666 chitin was slowly added. Due to gel solidification, the beaker was taken from the bath. As the material warmed, remaining chitin was stirred into the methanesulfonic acid by magnetic stir bar and glass rod. When the beaker was returned to the ice bath, 3.8 ml of p-toluoyl chloride was added to the mixture dropwise. Stirring was continuous but, again, the viscosity impeded blending. The reaction was completed in 30 minutes at room temperature.

The beaker was placed in a 5°-8°C bath for 5 hours. The mix was stirred and the viscosity of the reaction mixture decreased. Following this procedure, the beaker was placed in a Fisher Scientific Isotemp refrigerated circulator at -20°C overnight.

The resultant pink mixture was diluted with 500 ml of 3°C 0.2 μ m D.I. H₂O. A small amount of white precipitate formed. The mix was next filtered with a Büchner funnel and No. 1 Whatman paper. A fine, white powder resulted. The powder was washed with 4°C 0.2 μ m D.I. H₂O and resuspended in a 5 ml methanol and 50 ml ether solution. After stirring for one hour, the mixture was filtered and re-washed with ether. The sand colored final product was air-dried overnight. The final product was dark brown and the yield was 4.7%.

Several tests were run to study the solubility of the p-methylbenzoyl chitin (PMBC) with various organic solvents.

<u>Solvents</u>	<u>Results</u>
Butyl Acetate	Insoluble
Dimethyl Sulfoxide (DMSO)	Cloudy solution after sonication
Methyl Ethyl Ketone	Insoluble
Xylenes	Insoluble
Dimethyl Formamide (DMF)	Cloudy solution after sonication. Settled to 2 layers.

These tests used 2 ml of solvent to 0.01 gm of PMBC. All blends were sonicated for 40 minutes, except the PMBC/methyl ethyl ketone system. The DMSO and DMF mixes were immiscible with both the polyurethane and enamel paints. Corroborating results were shown on painted aluminum strips. Separate carrier agent investigations were run with butyl acetate- and toluene-DMSO and PMBC (1:1 v/v).

A refined procedure was therefore adopted. 10 gm of Sigma C-3387 chitin was dissolved in 70 ml of methanesulfonic acid at room temperature. The reaction was slightly exothermic and a dark brown mixture formed. Ease of stirring was significantly increased.

This material was placed in the 0°C ice bath and 38 ml of p-toluoyl chloride was added dropwise while stirring with both magnetic Teflon stirbar and rod. The reaction was initially exothermic and bubbling occurred. Water vapor was evident. The mixture was stirred for 3.5 hours and turned pink-brown.

The beaker was next placed in the refrigerated circulator bath and kept at -20°C for 36 hours. The frozen, pink-brown solid was washed with 0.5°C-250 ml 0.2 μ m D.I. H₂O. On addition of the ice water, the reaction was exothermic. The product was filtered using P4 Fisher filter paper and ice water wash. The off-white solids were resuspended in methanol/ether (1:10; v/v) and stirred for 1 hour. A pink, fine powder resulted and was rewashed with ether and filtered. The final PMBC product was off-white.

Several tests were run on the miscibility of PMBC and various organic solvents and paints. The solvent-solute mixtures were sonicated for 40 minutes before mixing with the polyurethane paint. The standard was 1 ml solvent with 1 ml polyurethane with 0.1 gm PMBC. The results were:

<u>Solvent</u>	<u>Dissolve PMBC</u>	<u>Miscible/Paint</u>	<u>Miscible/Paint/PMBC</u>
Thinner	Yes	Cloudy	Yes
MEK	No	Soluble	No
Toluene	No	No	No
Turpentine	No	No	No
Xylenes	No	No	No
Acetone	No	Soluble	No
Butanol	Yes	Yes	Yes
Butyl Acetate	No	Cloudy	Cloudy

PMBC was found soluble in butanol/DESOTO mil T-81772 thinner. Test variations are shown below:

Variation I Reagents

0.1 gm PMBC
0.5 ml Butanol
0.5 ml Polyurethane Paint
0.5 ml Thinner

Results and Comments

Appeared to be miscible on mixing, but settled to 2 layers. The coating on the aluminum strip resembled that of latex paint. It appeared to contain fine powder. The PMBC appeared only partially soluble in the paint.

Variation II Reagents

0.2 gm PMBC
0.5 ml Butanol
0.5 ml Polyurethane Paint
0.5 ml Thinner

Results and Comments

The increase in PMBC concentration increased the miscibility of the mixture. The coating on the aluminum strip did not contain fine powder. The PMBC appeared soluble in the paint. The strips showed icephobic and antifouling potential. The above test group does not correlate.

Variation III Reagents

0.4 gm PMBC
2 ml Butanol
1 ml Polyurethane Paint
2 ml Thinner

Results and Comments

Miscibility worse than above II reaction. Butanol appeared the reach its saturation point with 0.2 gm PMBC.

Variation IV Reagents

0.4 gm PMBC
2 ml Butanol
0.5 ml Polyurethane Paint
2 ml Thinner

Results and Comments

Miscibility worse than above II reaction.

Variation V Reagents

0.1 gm PMBC
1 ml Butanol
1 ml Enamel Paint

Results and Comments

Immiscible

The PMBC/butanol mix was soluble in polyurethane paint, dependent upon PMBC concentration. The testing mixes were painted on aluminum strips. These strips were studied under stereomicroscope. These strips also showed positive icephobic and antifouling potential. Work continues to find a "best-fit" solvent and/or carrier for PMBC.

RESULTS AND CONCLUSIONS

In Contract N00014-90-C0062, Technical Research Associates:

- o Verified the icephobic and antifouling potential of mechanically blended chitin/- and chitosan/paints.
- o Verified the icephobic and antifouling potential of chemically blended chitin/paints.
- o Determined the feasibility of chitin/paint mix biodegradation.

The project was divided into five tasks. Task I focused on the development of homogenous chitin or chitosan suspensions. Once the chitin and chitosan addition techniques were optimized, Task II work determined standard ASTM test characteristics. Tasks III, IV and V centered on the icephobic, antifouling and biostripping investigations.

Chitin and chitosan powders were purchased from seven sources. Each material was reduced to Tyler mesh screen sizes:

+20 (850 μm)
-20 to +80 (180 μm)
-80 to +100 (150 μm)
-100 to +200 (75 μm)
-200 to +325 (45 μm)
-325

Each reduced chitin or chitosan powder was then mechanically or chemically mixed in 3 polyurethane, 2 enamel and 2 latex paints. Weight percentages of 1, 2, 3, 4, 5, 10 and 20 were added, based on the percentage non-volatiles in each paint. Both grey and black as well as flat and glossy paints have been used, with and without primer. Dispersion was occasionally aided by preblending the chitin/chitosan fractions with paint thinner. The example matrix below, was followed for every type chitin/chitosan, Tyler screen size, use of primer and type paint:

<u>Tyler Mesh</u>	<u>Weight %</u>	<u>Paint</u>	<u>Color</u>	<u>Type</u>	<u>Primer</u>
Chitin A+20	1	polyurethane	Black	Flat	Yes
"	2	"	"	"	"
"	3	"	"	"	"
"	4	"	"	"	"
"	5	"	"	"	"
"	10	"	"	"	"
"	20	"	"	"	"

Experiments demonstrated:

A.

- o Mechanically-mixed, chitin/polyurethane coating systems are more icephobic than standard paint systems.
- o Dispersal percentages in the 10-15% range and mesh sizes of <-200 are optimum for icephobic qualities.
- o Ice repulsion on physically-dispersed chitin is satisfactory to -5°C but not to the required -35°C temperature.

B.

- o Successful chemically-modified chitin solutions and gels have been produced.
- o Miscibility of chemically-modified chitin solutions and gels with polyurethane, enamel and latex paints has been achieved.
- o Chemically-modified-chitosan latex paint dispersions have shown improved icephobicity but do not resist fungal attack.
- o Work continues to research miscible carrier agents for polyurethane paints.

C.

- o The -200 mesh chitin, polyurethane, black, glossy paints resist fungal attack.
- o Anti-fungal test results on other substrates show varying amounts of degradation on the chitin-based paints.
- o Enamel and polyurethane paints are preferred.

D.

- o Chitinase biodegradation experiments have been successful, but not timely.
- o Optimization continues.

E.

- o Physically-dispersed chitin or chitosan addition has increased the density and the drying time of the paint mixtures, as the percentage of powder increased.
- o The brushing, flow characteristics and consistency of the paints and primer were improved with chitin or chitosan addition.
- o The physical addition of chitosan to the primer aided paint/substrate cohesiveness.

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Appendix

Materials

2 phenoxy ethanol: 117-5223, Lot 807455A.
Eastman Kodak Co., Rochester, NY 14650

2-propanol. A516-4. Lot 854124.
Fisher Scientific. Fair Lawn, NJ 07410.

Acetic Acid. A38-500. Lot 882475 Fisher.

Acetic Anhydride. A10-1. Lot 902285. Fisher.

Acetone. A18-500. Lot 881801. Fisher.

Aluminum (8 mm--3003H14):
Bralco Aluminum Co., 8321 Cansord, Pico Rivera, CA 90660.

ANB-NOS 21551. Lot 891220081.
Pierce Chemical Co. Rockford, Ill. 61105.

AR Hcl: A144-212. Lot #897062. Fisher.

Butanol. A399-4. Lot 894164. Fisher.

Butyl Acetate CAT1168939. Lot A15A.
Eastman Kodak Co. Rochester, NY 14650.

CTC Chitin. Lot 00430A.
CTC Chitosan. Lot 00430B.
CTC Organics. PO Box 6933. Atlanta Georgia 30315.

Caproic Acid. H05450.
Pfaltz and Bauer. Waterbury, CT 06708.

Caprylic Acid. 001160. Pfaltz and Bauer.

DMF D119-500. Lot 902004. Fisher.

Desoto Super Desothane Aliphatic Polyurethane Enamel paint
(36270). DESOTO Inc., Chicago Heights, IL.

Desoto Activator MHS-420. Desoto Mil T-81772A Thinner.

EDC 22980 Lot 900502086. Pierce.

Ethanol (200 proof): DSP-111-418.
USI Chemicals Co., Tuscola, IL 61953

Ether--absolute, ACS reagent. 34,613-6. Lot #: 00117CW.
Aldrich Chemical Company. Milwaukee, WI 53233.

Ether: UN1155, Lot 0804 KCMJ.
 Mallinckrodt Chemical Works, Paris, KY 40361

Ethyl acetate: EXD240-5, Lot 5318.
 EM Science, 111 Woodcrest Rd., Cherry Hill, NJ 08034

Ethylene glycol: 5001, Lot VVK. Mallinckrodt.

Formaldehyde: 5016-500, Lot 4456 KCNV. Mallinckrodt.

Formamide: FX0420-3, Lot 7076. EM Science.

Glycerol (1:1 with H₂O): BP-229-1000, Lot 881437. Fisher.

HSAB 21560. Lot 900416083. Pierce.

Hexanes: HXo310-1, Lot 8022. Em Science.

Igepal. CO-720 (9016-45-9) Lot 00606MP. Aldrich.

Isopropanol. E141-4. Lot 893890-36. Fisher.

Linoleic Acid. L03440. Pfaltz and Bauer.

Methanesulfonic Acid--99% M860-6. Lot #:09307HX. Aldrich.

Methanol. A412-500. Lot 893537. Fisher.

Methyl Sulfoxide. 67-68-5 Lot 09231JW. Aldrich.

Methyl isobutyl ketone: M-213. Lot Z40183. Fisher.

Methylene chloride: D-150. Lot 857070. Fisher.

Methylsulfoxide: 22680. Lot 09231 JW. Aldrich.

Nonanoic Acid. N13570. Pfaltz and Bauer.

N-Valeric Acid. V00075. Pfaltz and Bauer.

Oleic Acid. 002610. Pfaltz and Bauer.

O-phosphoric Acid. A242-500. Lot 881213. Fisher.

p-toluoyl Chloride--98% 10,663-1. Lot #: 01425JW. Aldrich.

Pfaltz and Bauer C07632 Chitin.
 Pfaltz and Bauer, Waterbury CT 06708.

Protan Sea Cure 350. Lot CSN478 Chitin.
 Protan Sea Cure (+) 210 Chitosan. Lot CSN.403
 Protan, Inc. Portsmouth, NH 03801.

Red Devil Gloss Polyurethane Oil Enamel. Lot 0428.
 Red Devil Paint and Chemicals. Mount Vernon, NY 10550.

Rust-oleum Protective Coating. Flat Black 7776.
 Stops Rust® Brand. Lot 95081

Rust-oleum protective Coating. Smoke Gray 7786.
 Stops Rust® Brand. Lot 96031

Rust-oleum Thinner & Cleaner 7700
 Lots 93082, 80141

Sears Best Easy Living Interior Satin. 93934. Lot 17C200.
 Sears, Roebuck & Co. Chicago, Ill. 60684.
 Sears Weatherbeater Exterior Galvanize Al. 37254. 90B239.

Sigma C-3387. Lot 106F-7365. Chitin. Practical Grade.
 Crab Shell.

Sigma Chemical Company, PO Box 14508, St. Louis, MO 63178.

Sigma C-3641. Lot 107F-7115. Chitin. Purified Powder.
 Crab Shells.

Sigma C-8908. Lot 59F7265. Chitin. Purified Powder.
 Shrimp Shells.

Sigma C-4666. Lot 128F0202. Chitin. Practical Grade.
 Poly-N-acetylglucosamine. Crab Shell.

Sigma C-0792. Lot 19F-03911. Chitosan. Practical Grade.
 Crab Shell.

Sigma M-3150. Lot 47F0532. Methylglycol Chitosan.
 Chitosan-2-methoxyethyl ether. 90%.

Sigma C-1525-48F-4032. Chitinase. Activity 10-20 u/mg solid.
 Poly[1,4-β(2-acetoamido-2-deoxy-D-glucoside)]-glycoanohydrolase.

Sodium Hydroxide. S318-500. Lot 893102. Fisher.

Sodium Metasilicate. S-408. Lot 741715. Fisher.

Toluene. TX0735-1. Lot 6282.
 EM Science. Cherry Hill, NJ 08034.

Turpentine. SD-81. Lot 2271869.
 Klean-Strip, div. of W.M. Barr, Inc. Memphis, TN 38101-1879.

Whatman International Ltd., Maidston, England: #1 Filter paper.

Xylenes. XX0055-1. Lot 8245. EM Science.