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ANTI-ICING CHITIN COATING SYSTEM DEVELOPMENT

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Abstract

In the third quarter of this work, ASTM testing has provided a quantitative means for sample characteristic's evaluation. Shear and tensile icephobic strength tests have replaced the marine ice bath for more direct input on anti-icing properties. Chemical alteration of a new water based chitosan with the paint has shown promise for eliminating surface roughness throughout the sample. Preliminary anti-fungal tests results have shown different amounts of degradation on the chitin based paints (percentage dependent) and that enamel and polyurethane paints are less susceptible than the latex.

Identifiers/Open-Ended Terms:Chitin,
Chitosan,
Icephobic Paint,
Antifouling Paint,
Enzymatic Degradation, of Paint, (JS) ←AvailabilityDefense Technical Information Center
Bldg. 5, Cameron Station
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FORWARD

This Technical Report covers work performed on Contract N00014-90-C-0062, entitled " ANTI-ICING CHITIN COATING SYSTEM DEVELOPMENT", technically through July 1, 1990 through August 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. Both Mr. Craig T. Miller and Ms. Gor Lai were responsible for this quarter's icephobic, antifungal and enzymatic testing. Mr. Trung Chau was responsible for the EDX, X-ray diffraction and FTIR analysis.

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SUMMARY

Technical Objective:

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

Work Statement:

The project will be divided into five tasks. Task I will focus on the development of homogenous chitin or chitosan suspensions. Once the chitin and chitosan addition techniques are optimized, Task II work will determine the chitin/chitosan-paint suspensions standard ASTM test characteristics. Tasks III, IV and V will then center on the icephobic, antifouling and biostripping investigations.

Approach:

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

Third Report Work To Date:

Preliminary anti-fungal test results showed varying amounts of degradation from the chitin based paints. The stereo microscope is now being used to evaluate sample surfaces more closely. ASTM testing has provided a quantitative means for sample characteristic's evaluation. Shear and tensile icephobic strength tests have replaced the marine ice bath for more direct input on anti-icing properties. Chemical alteration of a new water based chitosan with the paint has shown promise for eliminating surface roughness throughout the sample.

INTRODUCTION

Several chitin and chitosan powders, varying from 20 to -200 mesh, have now been physically mixed with enamel, polyurethane and latex paints and primer in weight percentages from 1 to 20. These powders have also been successfully chemically modified and reacted with latex paint. Chitosan addition has been shown to be preferable with increased icephobic and antifungal properties.

Experimental evidence, however, indicates a need for a chemically-modified-chitosan dispersion. Miscibility of chitosan-modified solutions or gels with latex paint has been achieved but the first chitosan solutions or gels have not formed stable mixes with the polyurethane and enamel paints. TRA researcher, are continuing the search for both a stable gel and an organic carrier agent to be used with these paints.

Shear and tensile strength testing was run on the Instron 640 testing apparatus to furnish the quantitative data on icephobic characteristics. Shear strengths were taken by placing the standard test sample (8mm x 70mm Al), painted on both sides and frozen vertically in a salt or tap water one inch cube, in the Instron. The sample was pulled until free from the cube. Since the samples had chitosan physically dispersed, the tensile strength tests were run to eliminate the surface roughness variable of the shear strength tests. These tests were conducted by painting the surface of a 5 cm diameter disk and then freezing a two inch column of water above it (with a bolt and washer frozen in the middle suitable for attachment to the Instron). The disk was then threaded to a stationary base and the bolt was pulled vertically by the Instron. The -200 mesh chitosan mixes at higher loadings, showed the greater icephobic properties.

Anti-fungal test observations were made two weeks after physically-dispersed chitosan/paint samples were placed in ten-day old mixed fungus cultures. Paint bubbling and separation from the metal surface were the two substantial issues. A poor paint coating technique was the cause of some of the difficulties. The fungi were well attached to the chitin/paint surfaces in most cases, but not the -200 mesh chitosan/paint surfaces. Black paint was also slightly more resistant to the fungi and resisted fungal attack better than the gray paint.

ASTM testing has provided a good quantitative means for sample evaluation. Physical chitin or chitosan addition has increased the density and the drying time of the paint mixture, as the percentage of chitosan increased. The brushing and flow characteristics and consistency of the paint and primer were improved. The physical addition of chitosan to the primer also aided the paint/substrate cohesiveness.

PROCEDURES

Materials

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

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.	
Sears Best Easy Living Interior Satin.		93934. Lot 17C200.	
Sears, Roebuck & Co.	Chicago, Ill.	60684.	
Sears Weatherbeater Exterior Galvanize	Al.37254.	90B239.	
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.
ANB-NOS	21551.	Lot 891220081.	
	Pierce Chemical Co.	Rockford, Ill.	61105.
Butanol.	A399-4.	Lot 894164.	Fisher.
Butyl Acetate	CAT1168939.	Lot A15A.	
	Eastman Kodak Co.	Rochester, NY	14650.
Caproic Acid.	H05450.		
	Pfaltz and Bauer.	Waterbury, CT	06708.
Caprylic Acid.	001160.	Pfaltz and Bauer.	
DMF	D119-500.	Lot 902004.	Fisher.
EDC	22980	Lot 900502086.	Pierce.
HSAB	21560.	Lot 900416083.	Pierce.
Igepal.	CO-720 (9016-45-9)	Lot 00606MP.	
	Aldrich Chemical Co.	Milwaukee, WI	53233.
Isopropanol.	E141-4.	Lot 893890-36.	Fisher.
Linoleic Acid.	L03440.	Pfaltz and Bauer.	
Methanol.	A412-500.	Lot 893537.	Fisher.
Methyl Sulfoxide.	67-68-5	Lot 09231JW.	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.
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.
Xylenes.	XX0055-1.	Lot 8245.	EM Science.

Temperature of reaction were ambient and additional approaches have now been tested to prepare stable and uniform suspensions or dispersions of chitin and chitosan in the paint.

Anti-fungal Test Results

Anti-fungal test observations were made two weeks after physically-dispersed chitosan/paint samples were placed in the ten day old mixed fungus cultures. Paint bubbling and separation from the metal surface were the two substantial issues.

Aspergillus oryzae		Aspergillus niger	
10196		9642	
1	COMMENTS	1	COMMENTS
CONTROL-BT	fungi well attached	CONTROL-BT	bubbled
S2-BT-100-3	attached to sample	S2-BT-100-3	fungi well attached
S2-BT-100-5	paint separated	S2-BT-100-5	peeling; bubbled
2		2	
CONTROL-GT	bubbled; purplish tint	CONTROL-GT	extremely bubbled
PS-GT-45-5	paint separated	PS-GT-45-5	extremely bubbled
PS-GT-80-5	fungi well attached	PS-GT-80-5	peeling; bubbled
3		3	
PS-GT-100-5	paint separated	PS-GT-100-5	fungi well attached
CB-GT-100-5	fungi well attached	CB-GT-100-5	fungi well attached
CA-GT-100-5	not firmly attached	CA-GT-100-5	fungi well attached
4		4	
CA-GT-100-10	paint separated	CA-GT-100-10	peeling; well attached
P2-BT-100-1	discoloration on Al metal	P2-BT-100-1	fungi well attached
P2-BT-100-2	scratches off easily	P2-BT-100-2	bubbled; well attached
5		5	
CONTROL-BT	bubbled; well attached	CONTROL-BT	peeling; bubbled
P2-BT-100-4	fungi well attached	P2-BT-100-4	peeling; bubbled
P2-BT-100-5	fungi well attached	P2-BT-100-5	fungi well attached
6		6	
P2-BT-100-10	fungi well attached	P2-BT-100-10	fungi well attached
P2-BT-100-15	lg. surface area	P2-BT-100-15	peeling
S6-BT-100-3	paint separated	S6-BT-100-3	fungi well attached
7		7	
P2-BT-200-5	fungi well attached	P2-BT-200-5	slightly attached
S7-GT-100-5	paint separated	S7-GT-100-5	bubbled
S7-BT-100-5	fungi well attached	S7-BT-100-5	bubbled
8		8	
S7-GT-100-15	bubbled; paint separated	S7-GT-100-15	peeling
S7-BT-100-15	purplish tint	S7-BT-100-15	peeling
S7-BT-200-5	fungi well attached	S7-BT-200-5	tiny bubbles
9		9	
CONTROL-GT	paint separated	CONTROL-GT	peeling; bubbled
S7-GT-100-20	paint separated	S7-GT-100-20	fungi well attached
P2-BT-100-3	bubbled	P2-BT-100-3	peeling; bubbled

The black paint was slightly more resistant to the fungi and adhered to the aluminum test strips better than the gray paint which had fungi well attached to the paint surface in most cases. A poor paint coat was the cause of some of the difficulties. The following is a list of possible solutions for a more consistent coating:

Paint Coat Solutions

1. Primer pre-coat on bare Al test strips
2. Two coats of chitin/paint preblend
3. Paint entire sample (both sides, edges, and ends
4. Experiment with dipping process instead of brushing
5. Try painting with no thinner added
6. Concentrate on brushing in one continuous stroke
7. Evaluate each sample under the stereo microscope before any tests are conducted. Look for thin areas of paint as well as obvious open spaces.
8. Estimate and compare samples for percentage of chitin (dispersal %) aggregates over the entire sample. Discard samples with low/high dispersal percentages.
9. Begin ASTM testing while painting the samples.

These ideas were tested with varying degrees of success. The primer pre-coat is explained in the ASTM brushing properties of this report. Two coats were too massive for our purposes. Painting the entire sample helped to provide more uniform testing of the treated surface. Dipping the samples did not provide any noticeably different characteristics. Painting without thinner produced a thick, uneven surface. Brushing in one continuous stroke did exhibit a more congruent sample. The stereo microscope provided close examinations for better sample evaluations.

EDX

The following EDX information was recorded by Trung Chau working in conjunction with Dr. John Chandler at the Veterans Administration Medical Center, SLC, UT, SEM Laboratory:

PRIMER EDX

ELEMENT	SET 1 WT %	SET 2 WT %	SET 1 ATOMIC %	SET 2 ATOMIC %
Mg	5.79	5.69	13.93	13.89
Al	5.42	5.04	11.74	11.08
Ca	4.39	3.57	6.41	5.28
Ti	10.63	10.66	12.97	13.20
Cr	12.62	12.40	14.18	14.15
Sr	61.14	62.64	40.78	42.40
TOTAL:	99.99	100.00	100.01	100.00

COMMENTS: SET 1 and SET 2 values are taken from different areas of the sample at the same magnification.

BARE Al TEST STRIP EDX

ELEMENT	SET 1 WT %	SET 1 ATOMIC %
Al	96.51	98.19
Cr	2.44	1.29
Fe	1.05	0.52
TOTAL:	100.00	100.00

COMMENTS: The EDX was performed by John Chandler
The sample is the metal side of the PRIMER STRIP sample.

SEA SALT EDX

ELEMENT	SET 1 WT %	SET 2 WT %	SET 3 WT %
Na	9.58	10.61	37.44
Mg	13.70	11.63	10.14
Al	2.63	0.00	0.00
Si	3.16	0.00	0.00
P	2.50	0.00	0.00
S	5.71	8.58	1.98
Cl	50.61	55.27	46.06
K	4.11	5.42	4.03
Ca	8.00	8.49	0.35
TOTAL:	100.00	100.00	100.00

ELEMENT	SET 1 ATOMIC %	SET 2 ATOMIC %	SET 3 ATOMIC %
Na	13.10	14.80	46.28
Mg	17.71	15.35	11.85
Al	3.06	0.00	0.00
Si	3.54	0.00	0.00
P	2.53	0.00	0.00
S	5.60	8.58	1.76
Cl	44.87	50.02	36.93
K	3.31	4.45	2.93
Ca	6.27	6.80	0.25
TOTAL:	99.99	100.00	100.00

COMMENTS: SET 1 is sea salt, as is, low mag., many crystals.
SET 2 is dissolved sea salt dried on planchet,
low mag., center of dried circle.
SET 3 is the same as SET 2 except for higher
mag., ring edge of circle.

NOTE: For SET 2 and SET 3, the crystals were not totally
dissolved, but should not be a problem because the minute amount
of undissolved solids were dispersed and picked by eye dropper.

The PRIMER EDX chart shows that the primer consists mainly of Sr (~61%), Cr (~12%), and Ti (~10%). The BARE METAL EDX gives an indication of the percent AL (~97%) used in the test strip alloy. The ICE PPT EDX chart was taken from a sample collected from the marine bath after forming overnight on the stainless steel cooling coil. The ppt's elemental percentages compare with the ppt. formed in the SEA SALT EDX SET 3. This shows that the ice ppt. is not a contaminant as was first expected. The SEA SALT EDX (Instant Ocean aquarium salt) compared the original crystals with two different areas of a precipitate. The salt was dissolved in D.I. H₂O and allowed to dry on a planchet. The ppt. formed a circle. SET 2 recorded the center of the circle at low mag. and SET 3 recorded the ring edge at a higher magnification. More Na was shown on the outer edge while slightly more Cl was discovered at the center of the ppt. circle.

Physical and Test Results

1. Density Tests

The objective of this test was to evaluate the density of the paint and paint-chitin mixtures. Two approaches were used: i. The mass of each mixture was measured with a Sartorius four digit scientific balance using a 40 ml fixed volume. Data were placed in the equation $p=m/v$. The percentage chitin was 5 and 10; ii. An aluminum rod with known density was hung from a Mettler PJ 300 specific gravity balance and submerged into testing samples with unknown densities. The difference between air and sample weights was recorded and again, the equation $p=m/v$ was used to determine density. Mass was equaled to the difference in readings and the volume was equal to the volume of the aluminum rod.

Using CTC Organic Chitosan, the results were:

	0%	5%	10%
i. $p=kg/m^3$	0.928±0.006	0.947±0.005	0.965±0.002
ii. $p=kg/m^3$	0.967±0.003	0.986±0.004	1.003±0.006
% Difference	4%	4%	4%

Under the non-ideal laboratory conditions, the 4% difference between the two approaches was acceptable. As expected, the density of the paint mixture increased as the percentage of chitosan increased.

2. Adhesive Tape Test

The objective of this test was to determine paint/substrate adhesive strength. Different adhesive tapes were used to test the peeling characteristic of the painted samples. The enamel and polyurethane paint samples did not peel on testing with duct tape or Scotch tapes. The latex paint samples peeled on testing with both tapes. Paint and chitin/paint samples had identical performance.

3. Measurement of Dry-Film Thickness (ASTM Method D1005)

The thickness of the unpainted aluminum strip substrates was measured by a digital caliber. Paint coating was then applied to the strips. When dried, the thickness of the painted aluminum strips was measured again and the difference in the two readings was determined to be the thickness of the paint. Three readings were taken adjacent to one another on each film.

The results were as follows:

<u>Samples</u>	<u>Thickness (inch)</u>
P2-G-100-5	0.002+/-0.0004
P2-G-100-10	0.003+/-0.001
S6-GT-45-5	0.001+/-0.0004
S6-GT-45-10	0.003+/-0.0008
CONTROL-L	0.001+/-0.0002
S6-L-100-5	0.002+/-0.0004
S6-L-100-10	0.002+/-0.0003
CONTROL-G-D1	0.002+/-0.0004
P2-GT-100-D1-5	0.002+/-0.000
P2-GT-100-D1-10	0.002+/-0.0005
CONTROL-GT	0.0008+/-0.0004
PS-GT-100-5	0.0015+/-0.0009
PS-GT-100-10	0.003+/-0.0005
PS-GT-100-15	0.003+/-0.0005
CONTROL-G-D1	0.003+/-0.0005
P2-GT-100-D1-5	0.0025+/-0.00
P2-GT-100-D1-10	0.003+/-0.0004
CONTROL-E-D1	0.002+/-0.0005
S6-E-100-D1-5	0.004+/-0.0004
S6-E-100-D1-10	0.005+/-0.0004
CONTROL-L-D1	0.004+/-0.0005
S6-L-100-D1-5	0.005+/-0.0004
S6-L-100-D1-10	0.006+/-0.0005
CONTROL-E	0.001+/-0.000
S6-E-100-5	0.002+/-0.0006
S6-E-100-10	0.004+/-0.0004
CONTROL-G-D1-B1	0.005+/-0.0004

In conclusion, the addition of chitin/chitosan increased the film thickness.

4. Drying Time Test (ASTM Method D1640)

There are eight stages in the drying time test:

- a. Set to touch
- b. Dust free
- c. Tack free
- d. Dry
- e. Dry hard
- f. Dry through
- g. Dry to recoat
- h. Dry print-free

The "tack free" and "dry print-free" tests were not performed due to the lack of equipment. The procedures for the different stages were as follows:

a. Set to touch: To determine set-to-touch time, lightly touch the test film with the tip of a clean finger and immediately place the fingertip against a piece of clean, clear glass. Observe if any of the coating is transferred to the glass. The film is set-to-touch when it still shows a tacky condition, but none of it adheres to the finger.

b. Dust-free: Separate a number of individual fibers from a mass of absorbent cotton with the aid of tweezers. At regular drying intervals, drop several of the cotton fibers from a height of 1 in. onto the marked section of the film. The film is considered to have dried dust free when the cotton fibers can be removed by blowing lightly over the surface of the film.

d. Dry-to-touch: The film is considered dry when it no longer adheres to the finger and does not rub up appreciably when the finger is lightly rubbed across the surface.

e. Dry-hard: With the aid of the thumb resting on the test film and the forefinger supporting the test panel, exert a maximum downward pressure (without twisting) of the thumb on the film. Lightly polish the contacted area with a soft cloth. The film is considered dry-hard when any mark left by the thumb is completely removed by polishing.

f. Dry-through: Place the test panel in a horizontal position at a height such that when the thumb is placed on the film, the arm of the operator is in a vertical line from the wrist to the shoulder. Bear down on the film with the thumb, exerting the maximum pressure of the arm, at the same time turning the thumb through an angle of 90 deg. in the plane of the film. The film is considered dry-through when there is no loosening, detachment, wrinkling, or other evidence of distortion of the film.

Both enamel and polyurethane paints were used in the tests. The enamel paint had a slower drying time than the polyurethane in the beginning, but exceeded the polyurethane in the later stages. Increases in the percentage of chitin increased the drying rate of the samples.

5. Sedimentation

Chitin particles (S-2 chitosan: -45, -80, -100, -200 mesh, 0.1g) were dispersed in 50 ml tap water and allowed to settle under the influence of gravity. A few drops of methanol were added to the mixture to decrease flocculation. Four tests were run in separate beakers, each with a different mesh size. The settling rate decreased with decreasing mesh size. The samples were checked after 3 hours and again in two days. No observable change was found.

6. Size Distribution

The objective of this test was to study the size and shape of the chitin particles composing each powder. Nine tests were run: a) three controls; b) three with 5% Protan Seacure⁺ 350 chitosan, -100 mesh and c) three with 5% Protan Seacure⁺ 350 chitosan, -200 mesh. Latex, enamel and polyurethane paints were diluted with n-butyl acetate and used as substrates. Each mixture was placed on the Vortex Genie 2 for two minutes and then poured onto a vertical glass plate. After drying, the sample film was compared to the control film on the basis of undissolved particles, gloss and flow. The results were:

LATEX

<u>Control</u>	<u>-100 mesh</u>	<u>-200 mesh</u>
Paint did not dissolve in solvent.	Paint and chitosan did not dissolve.	Paint and chitosan did not dissolve.
No gloss.	Surface was rough.	Surface was not as rough as -100 mesh.

Flow was the same for all 3 plates

POLYURETHANE

<u>Control</u>	<u>-100 mesh</u>	<u>-200 mesh</u>
Streak marks	More obvious streak marks. Chitosan particles interrupted the flow of paint.	Chitosan particles helped to spread out the paint. The flow was even.
Glossy.	More glossy than the -200 mesh.	

ENAMEL

<u>Control</u>	<u>-100 mesh</u>	<u>-200 mesh</u>
Streak marks.	Streak marks.	Streak marks.
Undissolved particles.	Chitosan particles disturbed the flow of paint.	Chitosan particles interrupted the flow of paint, but because the size of particles was small, it helped to spread out the paint and held the color pigment.

The control samples continued to be more glossy than those containing chitin/chitosan and the -100 samples were more glossy than the -200 samples. The enamel samples were more transparent than either the latex or polyurethane paints, with and without chitin/chitosan. The addition of chitin/chitosan, however, helped distribute the paint more evenly on the glass plate.

7. Brushing and Sagging Properties, Consistency and Contact Angles

Painted samples were inspected with a stereo microscope. Coatings which had been dipped showed more sag at the bottom of the aluminum strip than did those which had been brushed. When "Sears aluminum primer" was painted on the aluminum strips before painting, sagging was decreased but roughness was increased. In general, chitin/chitosan was distributed evenly on the samples but air bubble formation was a problem in both dipping and brushing procedures. Of the three paints tested, the latex coating showed more air bubbles than the enamel or polyurethane and, as a consequence, peeled off easily from the aluminum.

The enamel paint samples were smoother than the polyurethane or latex samples. Final tests used a vacuum pump to remove the air from the paint before application. This procedure helped reduce the formation of air bubbles in the samples. Contact angles varied from 0 to 5 degrees.

Chemical Alteration

Additional tests have been run since those reported in report ONRC1 to test the miscibility of paint in various solvents. Enamel and polyurethane paints were immiscible with acetic acid but formed colloidal dispersions with sodium silicate. The two paints were also immiscible with concentrated aqueous phosphoric acid. In following tests, the two paints were mixed with caproic acid, linoleic acid, nonanoic acid, N-valeric acid and caprylic acid, respectively. At first, a dispersion was obtained, but the mixture gradually settled to 2 immiscible layers. Furthermore, CTC Organic chitosan was found insoluble in sodium silicate even when heated. The following are some of the results from the Protan Sea Cure Chitosan +210 water soluble chitosan tests:

<u>Solvent</u>	<u>WATER SOLUBLE CHITOSAN TESTS</u>	
	<u>Miscible with Thinner</u>	<u>Results</u>
phenoxy ethanol	no	partial colloidal suspension
200 proof ethanol	no	partial colloidal suspension
Desoto Mil T-81772A	yes	partial colloidal suspension
thinner		
ethyl acetate	yes	insoluble
ethylene glycol	no	insoluble
hexanes	yes	insoluble
methyl isobutyl	yes	insoluble
ketone		
Rust-oleum paint thinner		colloidal suspension
toluene	yes	partial colloidal suspension
turpentine	yes	insoluble
(steam distilled)		
xylenes	yes	partial colloidal suspension
aluminum primer	yes	partial colloidal suspension
acetone	yes	insoluble
oleic acid		partial colloidal suspension
3ml igepal CO-720		soluble
with 15ml water		
iso-propyl ether		insoluble
butanol	yes	
water	no	soluble
2-propanol		insoluble

10ml of solvent was mixed with 0.1g chitosan. Those mixtures miscible with thinner were sonicated for seven hours. No observable changes occurred.

Other attempts to mix the Protan water soluble chitosan and paint were made. Caproic acid, linoleic acid, nonanoic acid, N-valeric acid and caprylic acid were found miscible with water on addition of methyl sulfoxide. Methyl sulfoxide, however, was unsuccessful as a carrier between the organic solvent (paint) and the water-chitosan solutions. Caproic acid was further tested by reacting with 1-ethyl-3-(3-dimethylamino-propyl) carbodiimide-HCl (EDC) with polyurethane paint, enamel paint and N,N-dimethylformamide (DMF). 0.5 g of the Protan water soluble chitosan was dissolved in 10 ml of 0.2 μ m Nanopure water. EDC in ratios of ten, fifty and one hundred mole times chitosan was mixed with caproic acid and 10 times by volume of acid of DMF.

The results were:

<u>Mole Ratio</u>	<u>Enamel</u>	<u>Polyurethane</u>
10	immiscible	immiscible
50	immiscible	immiscible
100	immiscible	chitosan came out of solution

In addition to the tests described in the previous paragraphs, the reaction of chitosan with aqueous acetic acid was studied. Two equivalent ACH(4-azidophenyl-bound partially N-acetylated chitosan) solutions were prepared (Aiba). 0.5 g of water soluble chitosan was dissolved in 20ml of 2% aqueous acetic acid. The mixture was then diluted by 30ml methanol. 0.106 ml of acetic anhydride was added and the mixture was stirred overnight at room temperature. The next morning, 25 ml of 1.2% aqueous sodium hydroxide and 25ml of methanol were added to the mixture. Then 0.0575g of N-Hydroxysuccinimidyl-4-azidobenzoate (HSAB) was added and the mixture was stirred for a few days at room temperature. The mixture was then poured into a 4% NaOH/methanol solution (1:1,v/v) and a gel formed. It was washed with water/methanol (1:1, v/v) and dried. The material was then dissolved in 2% aqueous acetic acid and then diluted with a five fold volume of methoxyethanol to produce an ACH solution.

Another ACH solution was prepared with the same approach using N-5-Azido-2-nitrobenzoyloxy-succinimide(ANB-NOS) instead of HSAB. However, both ACH solution were immiscible to enamel and polyurethane paints. Nevertheless, the gelation characteristic of chitosan with acetic acid was noticed and further investigation followed. The same approach of making an ACH solution without the addition of methoxyethanol, HSAB or ANB-NOS was used to prepare a chitosan gel. The gel was then put into different organic solvents which are miscible with paints. The results were:

Chitosan Gel With Organic Solvents

<u>Solvents</u>	<u>Solubility</u>
butyl acetate	insoluble
toluene	insoluble
xylenes	insoluble

Vortex and ultrasonic were used to attempt to break down the gel into solution.

Another approach of preparing the chitosan gel was also used (Teixeira). 2.5g of Sigma C-0792 chitosan, -45+80 mesh, was added to 50ml of 10% acetic acid and left overnight. The solution was then diluted with 200ml of methanol and stirred for several hours, then filtered. A 1% w/v chitosan solution was produced. Acetic anhydride was added to the filtered solution at 1/30 of the total volume. The gel formed was transferred to a glass petri dish, washed twice with acetone and left to air dry overnight. The dried gel was then tested with different organic solvents:

Chitosan Gel with Organic Solvents

<u>Solvents</u>	<u>Solubility</u>
butyl acetate	insoluble
toluene	insoluble
xylenes	insoluble

Vortex and ultrasonic were used to help to break down the gel into solution.

Icephobic Strength Tests

The Marine Bath Freeze Tests explained in report ONRC2 (6/30/90), pg. 8, have not provided satisfactory quantitative analysis of the paint systems' icephobic properties. Shear and tensile strength testing has begun on the Instron 640, Canton, MA testing apparatus. This equipment has furnished quantitative data on icephobic characteristics (Figure 1).

Shear strengths were taken by placing the standard test sample (8mm x 70mm Al) painted on both sides and freezing them vertically in a salt or tap water one inch cube. After freezing they were placed in the Instron and pulled until free from the cube. The Instron was calibrated between 0-10kg. The following table lists the data converted to english units:

SHEAR STRENGTH TESTS

<u>SAMPLE</u>	<u>LOAD</u> (LBS.)	<u>SHEAR STRENGTH</u> (PSI)
50 g/L SALT H2O -20oC FOR 24 HRS.		
PS-GT-100-5	6.0	8.9
PS-GT-100-10	5.1	7.6
PS-GT-100-15	8.6	12.9
BARE ALUMINUM	3.5	5.3
CONTROL-GT	1.4	2.1
TAP H2O		
S6-E-100-5	10.1	19.0
S6-E-100-10	16.1	30.2
S6-P-E-100-5	13.7	25.6
S6-P-E-100-10	19.0	35.6
TAP H2O		
CONTROL-G-D1	3.3	6.2
CONTROL-G-D1	8.2	15.3
CONTROL-L-D1	17.6	33.2
CONTROL-L-D1	22.1	41.4
CONTROL-E	12.4	23.2
CONTROL-E	14.6	27.4
CONTROL-P-E	15.7	29.4
CONTROL-P-E	14.1	26.5
CONTROL-E	17.4	32.7
CONTROL-E	13.7	25.7

These samples had chitin/chitosan physically dispersed in the paint. The shear strength tests show that a) more force is required to pull the samples from the tap water. b) the BARE Al and the Control-GT samples required less force than the chitin painted samples. c) the higher dispersal percentage, more force (less icephobic) was needed to free each sample. Observations made during the testing indicate the shear strength readings were more dependent on the surface roughness of each sample rather than the icephobic properties of the paint system.

Tensile strength tests will eliminate the surface roughness variable of shear strength testing. Tensile tests were conducted by painting the surface of a 5cm dia. disk and freezing a two inch column of water above it with a bolt and washer frozen in the middle suitable for attachment to the Instron. The 5cm dia. disk was threaded to a stationary base and the bolt was pulled vertically by the Instron. The following data was recorded:

TENSILE STRENGTH TESTS

<u>SAMPLE</u>	<u>LOAD</u> (LBS.)	<u>TENSILE STRENGTH</u> (PSI)	<u>NOTES</u>
BARE Al	2.5	0.82	ICE MELTED
WS-GT-200-10	7.7	2.53	ICE BROKE
CONTROL-GT	13.9	4.57	" "
WS-GT-200-10	8.8	2.89	GOOD SEPARATION
BARE Al	12.8	4.21	ICE BROKE
WS-GT-200-10	22.5	7.39	" "
BARE Al	8.2	2.68	GOOD SEPARATION
CONTROL-GT	15.0	4.93	ICE BROKE
WS-GT-200-5	9.7	3.19	" "
CONTROL-GT	12.8	4.20	" "
WS-GT-200-5	19.0	6.23	" "
BARE Al	4.4	1.45	" "

The ice melting or breaking instead of cleanly separating from the ice/paint interface was a problem during this test. More samples need to be run with different chitin/chitosan/paint combinations before substantial conclusions can be stated.

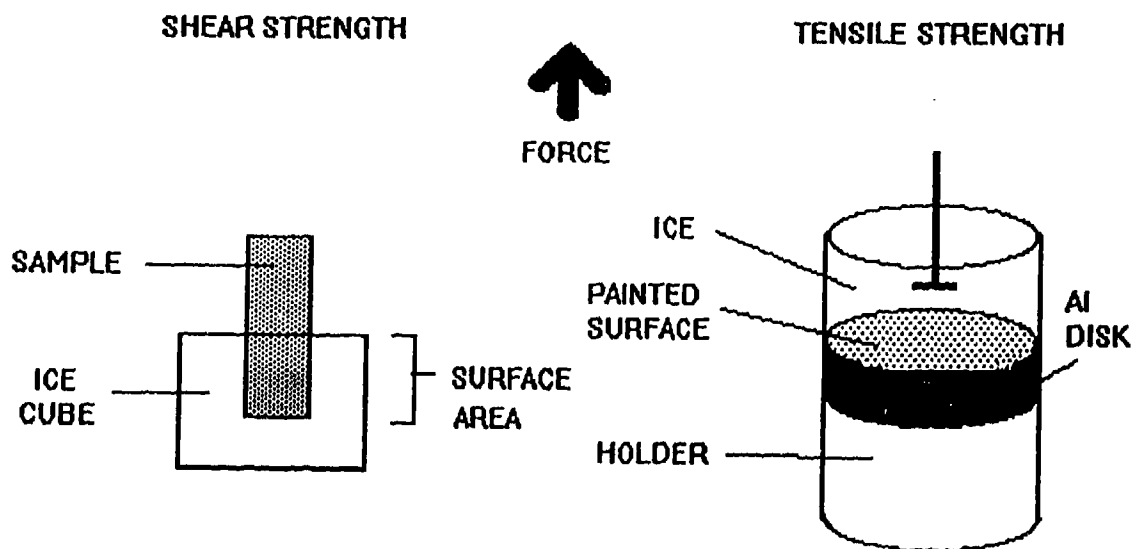


FIG. 1

X-RAY Diffraction

X-ray diffraction of painted aluminum strips was obtained by modifying a powder diffraction method. The conventional powder specimen holder was used to hold the painted strips as shown in Figure 2 below. The strips (approximately 0.016 inches thick) were held in place by applying Scotch tape at the two end. The strips were then scanned as if they were powder specimens. This modified method had been tested before at TRA, where graphite fibers were held in place as described. The peaks obtained matched known values. The spectra for the painted strips are very distinct. The X-ray diffraction parameters are:

Voltage:	35 kV
Current:	15 mA
Source:	CuK (alpha) radiation - no filter wavelength = 1.5418×10^{-10} m
Scan rate:	1 degree/minute
Chart rate:	1 inch/minute
Scale:	1 degree/inch (0.1 inch increments)
Scan range:	5 to 35 degrees

The peaks were tabulated into d-spacings by applying Bragg's law of diffraction:

$$d = \lambda / [2 \times \sin(\theta)]$$

λ = wavelength = 1.5418×10^{-10} m
 θ = angle of diffraction
 d = plane spacing

The peak intensities are recorded as heights in inches.

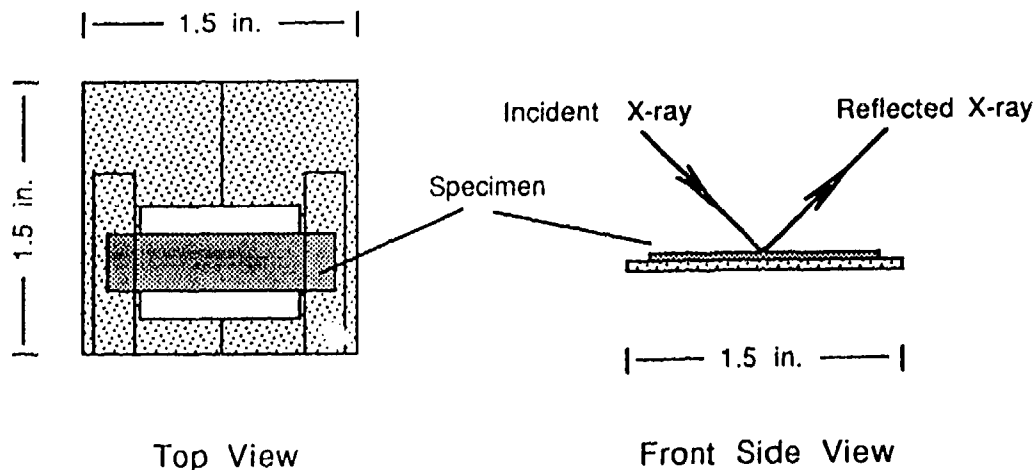


Figure 2

Control E.XRD

XRD Results

Scanned: 8/11/90

Sample: Control E

2theta start: 10 degree

Scan rate: 2.0 deg/min

2theta end: 70.0

Chart speed: 1.0 in/min

CuK (alpha) radiation

Scale: 2 deg/in

wavelength: 1.5418 A

 $d = \text{wavelength} / 2\sin(\theta)$

2theta (deg)	Intensity (in)	theta (deg)	theta (rad)	d (A)	Rel. Intensity
27.8	1.7	13.9	0.243	3.21	2.0
29.8	0.1	14.9	0.260	3.00	0.1
36.5	0.8	18.3	0.319	2.46	0.9
38.8	0.5	19.4	0.339	2.32	0.6
39.5	0.1	19.8	0.345	2.28	0.1
41.6	0.4	20.8	0.363	2.17	0.5
41.7	0.2	20.9	0.364	2.17	0.2
43.8	0.2	21.9	0.382	2.07	0.2
44.4	0.4	22.2	0.387	2.04	0.5
45.0	7.7	22.5	0.393	2.01	8.9
54.6	1.0	27.3	0.476	1.68	1.1
57.0	0.3	28.5	0.497	1.62	0.3
63.0	0.2	31.5	0.550	1.48	0.2
64.3	0.2	32.2	0.561	1.45	0.2
64.5	0.2	32.3	0.563	1.44	0.2
65.4	8.7	32.7	0.571	1.43	10.0
65.6	5.4	32.8	0.572	1.42	6.2
69.3	0.3	34.7	0.605	1.36	0.3

Control G.XRD

XRD Results

Scanned: 8/11/90

Sample: Control G

2theta start: 10 degree

Scan rate: 2.0 deg/min

2theta end: 70.0

Chart speed: 1.0 in/min

CuK (alpha) radiation

Scale: 2 deg/in

wavelength: 1.5418 A

 $d = \text{wavelength} / 2\sin(\theta)$

2theta (deg)	Intensity (in)	theta (deg)	theta (rad)	d (A)	Rel. Intensity
27.9	1.1	14.0	0.243	3.20	1.6
29.2	0.1	14.6	0.255	3.06	0.1
30.0	0.8	15.0	0.262	2.98	1.1
30.1	0.2	15.1	0.263	2.97	0.3
30.6	0.1	15.3	0.267	2.92	0.1
36.0	0.3	18.0	0.314	2.49	0.4
36.6	0.5	18.3	0.319	2.46	0.7
38.9	0.4	19.5	0.339	2.32	0.6
41.8	0.3	20.9	0.365	2.16	0.4
42.0	0.2	21.0	0.367	2.15	0.3
43.6	0.2	21.8	0.380	2.08	0.3
43.9	0.2	22.0	0.383	2.06	0.3
44.7	0.3	22.4	0.390	2.03	0.4
44.8	0.3	22.4	0.391	2.02	0.4
45.2	6.0	22.6	0.394	2.01	8.6
48.0	0.1	24.0	0.419	1.90	0.1
49.0	0.1	24.5	0.428	1.86	0.1
54.7	0.7	27.4	0.477	1.68	1.0
57.0	0.2	28.5	0.497	1.62	0.3
63.1	0.2	31.6	0.551	1.47	0.3
64.5	0.2	32.3	0.563	1.44	0.3
65.5	7.0	32.8	0.572	1.43	10.0
65.7	4.5	32.9	0.573	1.42	6.4
69.4	0.2	34.7	0.606	1.35	0.3

P2-G-10.XRD

XRD Results

Scanned: 8/11/90

Sample: P2-G-10

2theta start: 10 degree

Scan rate: 2.0 deg/min

2theta end: 70.0

Chart speed: 1.0 in/min

CuK (alpha) radiation

Scale: 2 deg/in

wavelength: 1.5418 A

 $d = \text{wavelength} / 2\sin(\theta)$

2theta (deg)	Intensity (in)	theta (deg)	theta (rad)	d (A)	Rel. Intensity
27.7	1.0	13.9	0.242	3.22	1.5
29.7	0.6	14.9	0.259	3.01	0.9
29.8	0.3	14.9	0.260	3.00	0.5
30.4	0.1	15.2	0.265	2.94	0.2
35.8	0.3	17.9	0.312	2.51	0.5
36.4	0.6	18.2	0.318	2.47	0.9
38.8	0.4	19.4	0.339	2.32	0.6
39.7	0.1	19.9	0.346	2.27	0.2
41.6	0.3	20.8	0.363	2.17	0.5
41.8	0.1	20.9	0.365	2.16	0.2
43.4	0.2	21.7	0.379	2.08	0.3
43.8	0.2	21.9	0.382	2.07	0.3
44.6	0.3	22.3	0.389	2.03	0.5
45.0	6.4	22.5	0.393	2.01	9.8
48.0	0.2	24.0	0.419	1.90	0.3
49.0	0.1	24.5	0.428	1.86	0.2
54.6	0.6	27.3	0.476	1.68	0.9
56.9	0.2	28.5	0.497	1.62	0.3
57.2	0.1	28.6	0.499	1.61	0.2
63.0	0.1	31.5	0.550	1.48	0.2
64.3	0.1	32.2	0.561	1.45	0.2
65.3	6.5	32.7	0.570	1.43	10.0
65.4	4.2	32.7	0.571	1.43	6.5
69.7	0.2	34.9	0.608	1.35	0.3

S6-E-100.XRD

XRD Results

Scanned: 8/11/90

Sample: S6-E-100

2theta start: 10 degree

Scan rate: 2.0 deg/min

2theta end: 70.0

Chart speed: 1.0 in/min

CuK (alpha) radiation

Scale: 2 deg/in

wavelength: 1.5418 A

 $d = \text{wavelength} / 2\sin(\theta)$

2theta (deg)	Intensity (in)	theta (deg)	theta (rad)	d (A)	Rel. Intensity
27.9	1.7	14.0	0.243	3.20	2.0
29.8	0.1	14.9	0.260	3.00	0.1
36.5	0.8	18.3	0.319	2.46	1.0
38.9	0.5	19.5	0.339	2.32	0.6
39.6	0.1	19.8	0.346	2.28	0.1
41.6	0.4	20.8	0.363	2.17	0.5
41.9	0.1	21.0	0.366	2.16	0.1
43.2	0.1	21.6	0.377	2.09	0.1
43.9	0.2	22.0	0.383	2.06	0.2
44.5	0.3	22.3	0.388	2.04	0.4
45.2	8.3	22.6	0.394	2.01	10.0
54.7	0.9	27.4	0.477	1.68	1.1
57.0	0.3	28.5	0.497	1.62	0.4
63.2	0.2	31.6	0.552	1.47	0.2
64.5	0.2	32.3	0.563	1.44	0.2
64.7	0.2	32.4	0.565	1.44	0.2
65.4	7.7	32.7	0.571	1.43	9.3
65.6	4.9	32.8	0.572	1.42	5.9
69.4	0.4	34.7	0.606	1.35	0.5
69.6	0.2	34.8	0.607	1.35	0.2

Results and Conclusions

Anti-fungal test results have shown that enamel and polyurethane paints are preferred over the latex. Paint bubbling and separation are being corrected by producing more uniform and complete sample coverage. Stereo microscopic evaluations confirm the improved paint application systems. EDX provided an elemental view of the salt used in the marine bath system. ASTM tests have furnished an overview on the physical properties of each paint application stage. Testing of the paint before, during and after applying to each test strip has given useful information on the chitin/chitosan-paint premix systems. Chemical alteration of standard chitin/chitosan and water soluble chitosan has not been stabilized in the paint system up to this point. New chemicals and procedures will be examined to establish a stable mixture. Shear and tensile strength tests have provided quantitative results on the icephobic properties of the paint system. A modified powder diffraction method was used to obtain x-ray diffraction data on the painted aluminum strips. Analysis of new products and testing methods will continue.

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