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REPORT NUMBER ONRC1

ANTI-ICING CHITIN COATING SYSTEM DEVELOPMENT

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Authors

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Performing Organization

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Project Scientist

Commander Steve Snyder

Abstract

The objectives of this ONR 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. The work will first focus on the production of homogenous chitin or chitosan suspensions. To date, five chitin/chitosan materials have been mixed with polyurethane paint in Tyler mesh screen fractions ranging from +20 (850 μm opening) to -200 (75 μm opening). Maceration techniques still require refinement. These powders have been added in 1, 2, 3, 4 and 5 weight percentages, based on the percentage non-volatiles in the paint. Dispersion was aided by preblending the chitin/chitosan fractions with paint thinner. Dispersion tests with seventeen other solvents proved unsuccessful. The most successful dispersion, to date, appears to be the -200 mesh (1-5 wt.%) Pfaltz and Bauer C07632 chitin/paint thinner preblend system. Preliminary icephobic tests are under way.

Identifiers/Open-Ended Terms

Chitin
Chitosan
Icephobic Paint
Antifouling Paints, (ref) ←
Enzymatic Degradation of Paint

Availability

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

Security Class

Unclassified
Unlimited

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FORWARD

This Technical Report covers work performed on Contract NO0014-90-C-0062, entitled " ANTI-ICING CHITIN COATING SYSTEM DEVELOPMENT", technically through February 1, 1990 through April 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 Commander Steve Snyder.

Mrs. Gail Bowers-Irons was both the Project Manager and Principal Investigator. Both Mr. Craig Miller and Mr. Robert Pryor were responsible for the maceration and mixing of chitin and chitosan into paint as well as the icephobic, antifungal and enzymatic testing

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.

First Report Work To Date:

Five chitin/chitosan materials have been mixed with polyurethane paint in Tyler mesh screen fractions ranging from +20 (850 μm opening) to -200 (75 μm opening). Maceration techniques still require refinement. These powders have been added in 1, 2, 3, 4 and 5 weight percentages, based on the percentage non-volatiles in the paint. Dispersion was aided by preblending the chitin/chitosan fractions with paint thinner. Dispersion tests with seventeen other solvents proved unsuccessful. The most successful dispersion, to date, appears to be the -200 mesh (1-5 wt.%) Pfaltz and Bauer C07632 chitin/paint thinner preblend system. Preliminary icephobic tests show the chitin coating system to be substantially better than standard paint in anti-icing properties. However, ice repulsion is not 100% at this time. More studies will be completed on chitin/chitosan types and percentages to aid in icephobic qualities.

INTRODUCTION

Two of the most important properties required of any protective coating system which has to withstand long term immersion in sea water are resistance to icing and fouling. Ice under natural conditions will not react chemically with admixtures, and is therefore difficult to eliminate. The majority of antifouling paints and coatings incorporate toxins which work by slowly migrating to the surface of the coating and subsequently forming a lethal concentration of toxin in the surrounding water.

Unfortunately, the lifetime of most coatings and icephobic and antifouling additives is short (<15 months) or inconsistent, due to sensitivity to solar radiation, weak adhesion to coated surfaces or condition of the protected surface, changes in the hydrometeorological conditions or over-leaching. Removal of paint is also expensive, time-consuming and potentially hazardous.

Further research is needed to find a more stable and consistent additive. Chitin is a white crystalline polysaccharide insoluble in water, dilute acids, cold alkalis of any concentration, and organic solvents but can be dispersed in hot concentrated solutions of neutral salts capable of a high degree of hydration. Chitosan is easily prepared by N-deacetylation of chitin. Chemically modified chitosans impart improved antistatic, soil repellent and soil release properties. Chitosan solutions have been found to be general in application and to develop decided strength and water resistance when thoroughly dried, heated or chemically treated.

Technical Research Associates, Inc. (TRA) believes that chitin or chitosan may be used both icephobically and antiseptically. This project would incorporate a chitin or chitosan suspension in paint and could provide a Mil Spec icephobic, antifouling and biodegradable coating that would be long-lasting, compatible and invariable.

PROCEDURES

Pre-contract Tests

In preliminary examinations, 1%, 2% and 3% (wt./wt.) of prepared Pfaltz and Bauer C07632 chitin was stirred directly (via Corning stir plate) into a 100 ml beaker containing Desoto Super Desothane Aliphatic Polyurethane Enamel paint (36270) and Desoto Activator MHS-420. The chitin was prepared following Archives of Biochem. Biophysics III., pp. 358-364, 1965: Fifty gm of technical grade shellfish chitin was transferred to a 500 ml beaker with 500 ml Fisher AR HCl while stirring. A Corning stir/hot plate was used and the solution turned syrupy, black brown. The solution was then heated to 30°C. Stirring continued until the solution became smoothly viscous.

The solution was then filtered through glass wool to another 500 ml beaker. Five hundred ml of 50% aqueous ethanol was added with vigorous stirring; this solution turned a light turbid brown. Number 1 Whatman paper was used to filter the solution. The precipitate was washed with 0.2 μ m Nanopure water and dried at room temperature. The final product was a brown semi-glossy granule that turned sandy brown upon grinding. A yield of 12.3 gm was shown. Grinding was not quantified.

Bralco Aluminum strips (8 mm x 70 mm Aluminum--3003H14) were painted with the chitin/paint coating and then air dried for 5 hours. They were then dried in an oven at 85°C for 90 hours. Mixing and dispersion was uneven. Following this treatment, the chitin/paint coating was tested for icephobic and algicidic characteristics. Strips of unpainted aluminum and control (no chitin) painted aluminum froze to the ice substrate in a refrigerator freezer. Strips painted with 1, 2 and 3% chitin/paint did not freeze to the substrate and actually repelled water and ice. Two and 3% chitin/paint samples killed algae cultures.

Start-up

Other approaches have now been tested to prepare stable and uniform suspensions or dispersions of chitin and chitosan in the paint. Temperature of reaction were ambient. In addition to the above materials, the following Sigma Chemical Company chitins have been tested:

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

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%.

Each chitin and chitosan product was put through a Tyler mesh screen series to separate the material according to particle size. The series contained:

| <u>Tyler Number</u> | <u>Opening</u> |
|---------------------|-------------------|
| 20 | 850 μm |
| 45 | 355 μm |
| 80 | 180 μm |
| 100 | 150 μm |
| 200 | 75 μm |

In order to obtain the higher Tyler screen fractions, materials were pulverized via either 1) Caulk Dentsply Vari-Mix III Amalgamator or Liquid Nitrogen freezing/mortar and pestle or blender reduction. Once macerated and sieved, the chitin was placed in the paint. The paint and thinner used in these first experiments included:

| | |
|--|-------------------------------|
| Rust-oleum Protective Coating. Stops Rust* Brand. | Flat Black 7776. Lot 95081 |
| Rust-oleum protective Coating. Stops Rust* Brand. | Smoke Gray 7786. Lot 96031 |
| Rust-oleum Thinner & Cleaner | 7700 Lots 93082, 80141 |

Percent non-volatiles were determined for the Rust-oleum paints to assure accurate chitin/chitosan loading. Six aluminum boats were weighed, covered with a layer of paint (three Flat Black 7776 and three Smoke Gray 7786) and re-weighed. The paint was first dried in a fume hood for 24 hours under ambient temperature conditions and then oven-dried at 75°C for 72 hours (until constant weight was achieved). Average percent paint was determined to be 66.430% for Flat Black 7776 and 52.046% for Smoke Grey 7786.

Mixing Tests

Forty ml of Rust-oleum Flat Black 7776 paint and 0.265 gm (1% based on percent non-volatiles) of the -45 + 80 fraction Sigma C-3387 chitin were mixed in a 100 ml disposable plastic beaker with a Brinkmann Kinematica Ag Polytron PT-MR-3000 homogenizer and Aggregate PT-OA 3012/2 at rpm's ranging to 20,000. Splattering and/or bubbling potential of paint, mixing efficiency and heat generation were determined. Heat was generated after several minutes although the aggregate remained cool. This mix was painted onto the 8 mm x 70 mm aluminum strips. In all cases, no-chitin controls were run. The chitin particles were easily observed as a bumpy (aggregated) surface. Ten ml of the Rust-oleum thinner was then added to the above mixture and homogenized through the range to 20,000 RPM. The viscosity of the paint was reduced and mixing increased. It was determined that 13,000 RPM was optimal (good mixing vs. no splattering or bubbling). Forty ml of Rust-oleum Flat Black 7776 paint was next mixed with 10 ml of Rust-oleum thinner in a 100 ml disposable plastic beaker with each remaining chitin and chitosan sieved fraction in 1, 2, 3, 4, and 5 weight percentages. These mixes were painted on the 8 mm aluminum strips but aggregation (clumping) remained a problem.

Several other mixing techniques were used. Sigma C-3387 chitin (0.266 gm-1%, -45 +80 fraction) was placed in a test tube with 4.0 ml paint thinner. The test tube was placed in a Branson 2200 ultrasound water bath (Branson Ultrasonics Corp., Eagle Road, Danbury, CT 06810-1961) for one minute. The mixture was stirred into a 100 ml disposable plastic beaker with 40 ml of Flat Black 7776 paint at 13,000 RPM with the Brinkmann homogenizer. The 8 mm x 70 mm aluminum strips were painted and aggregation occurred. The disposable beaker was then placed in the Branson ultrasound bath for 10 minutes. Aluminum strips were again painted, with dispersion slightly improved. Tests were run with both Pfaltz and Bauer CO-7632 and Sigma C-3387 chitin -100 + 200 fraction at 1, 2 and 3 weight percentages-40 ml Flat Black paint and 5 ml thinner. The samples were painted on the 8 mm x 70 mm Bralco aluminum strips and the Pfaltz and Bauer CO-7632 showed slightly better dispersion than the Sigma C-3387 samples. A test with Sigma M-3150 Methylglycol chitosan (90% chitosan 2-methoxy ether) mixed 40 ml of the Flat Black paint and 5 ml of thinner with 0.91% (0.243 gm) material. Particle size was unknown. Distinctive bumps were noticeable on the paint surface before and after drying.

First non-aggregated dispersions were shown with a -200 mesh fraction of Pfaltz and Bauer CO-7632 chitin at a 1%-0.266 gm loading added to a mixture of 40 ml Flat Black Paint and 5 ml thinner in a 100 ml disposable plastic beaker at 13,000 RPM. Identically tested Sigma C-3387 chitin -200 mesh fractions at 1, 2, 3, 4 and 5 weight percentages also showed good dispersion.

Further tests preblended Sigma chitin C-3387 (0.1 gm of -45 +80 mesh) with 5 ml of the following solvents. A list of catalogue and lot numbers with addresses is given in the appendix. Rust-oleum paint thinner was used as standard and a Vortexer was used to mix materials in 16 mm x 100 mm glass test tubes.

TABLE I

| <u>Solvent</u> | <u>Miscible with Thinner</u> | <u>Coagulation</u> |
|--------------------------------------|------------------------------|--------------------|
| 0.2 μ Nanopure H ₂ O | No | Yes |
| 2 phenoxy ethanol | No | Yes |
| 200 proof ethanol | No | Yes |
| DESOTO Mil T-81772A thinner | Yes | No |
| ether | - | No |
| ethyl acetate | Yes | No |
| ethylene glycol | No | Yes |
| formaldehyde | No | Yes |
| formamide | No | Yes |
| glycerol (1:1 with H ₂ O) | No | Yes |
| hexanes | Yes | Yes/fibrous |
| methyl isobutyl ketone | Yes | No |
| methylene chloride | - | No |
| methylsulfoxide | No | Biphasic |
| Rust-oleum paint Thinner | | No |
| toluene | Yes | Yes/fibrous |
| Turpentine (steam distilled) | Yes | No |
| xylenes | Yes | No |

The ethanol and 2 phenoxy ethanol mixes produced a good dispersion of chitin but did not yield a non-aggregated paint. The ethylene glycol mix was too thick. Once painted, the ethyl acetate samples were poor.

Final tests in this group of tests examined 8 mm x 70 mm painted aluminum strips with -200 mesh chitin and chitosan in 1-5% dispersals. The polymers were again added to 40 ml of Flat Black paint and 5 ml thinner in a 100 ml disposable plastic beaker and mixed at 13,000 RPM by the Brinkmann homogenizer. Although all samples appeared to have good dispersion, without aggregation, the Pfaltz and Bauer CO-7632 chitin was considered most favorable. Table II shows a complete list of most recent experiments.

TABLETT.XLS

| A | B | C | D | E | F |
|--------|--------------|---------------------|---------------------|---------|--------------------------|
| SAMPLE | TYPE | PAINT MIX | MESH | DISP. % | COMMENTS |
| 1 | S7-B-45-1 | SIGMA C'IN C-3387 | 40ml B only | 1 | aggregates too large |
| 2 | S7-BTU-45-1 | SIGMA C'IN C-3387 | 8+5ml TH+10m US | 1 | aggregates too large |
| 3 | S7-BTU-45-2 | SIGMA C'IN C-3387 | 8+5ml TH+10m US | 2 | aggregates too large |
| 4 | S7-BT-80-1 | SIGMA C'IN C-3387 | 40ml B+10ml TH | 1 | aggregates too large |
| 5 | S7-BT-80-2 | SIGMA C'IN C-3387 | 40ml B+10ml TH | 2 | aggregates too large |
| 6 | S7-BT-80-3 | SIGMA C'IN C-3387 | 40ml B+10ml TH | 3 | aggregates too large |
| 7 | SO-BT-7-.91 | METHYLGLYCOL C'SAN | 40ml B+10ml TH | 0.91 | aggregates too large |
| 8 | P2-BEA-100-1 | PFALTZ & BAUER C'IN | 8+5ml ethyl acetate | 1 | did not reduce agg. size |
| 9 | CONTROL-8T | NONE | 40ml B+10ml TH | *** | paint +thinner only |
| 10 | S7-BT-100-1 | SIGMA C'IN C-3387 | 40ml B+10ml TH | 1 | aggregates too large |
| 11 | S7-BT-100-2 | SIGMA C'IN C-3387 | 40ml B+10ml TH | 2 | aggregates too large |
| 12 | S7-BT-100-3 | SIGMA C'IN C-3387 | 40ml B+10ml TH | 3 | aggregates too large |
| 13 | S7-BT-100-4 | SIGMA C'IN C-3387 | 40ml B+10ml TH | 4 | aggregates too large |
| 14 | S7-BT-100-5 | SIGMA C'IN C-3387 | 40ml B+10ml TH | 5 | aggregates too large |
| 15 | P2-BT-100-1 | PFALTZ & BAUER C'IN | 40ml B+10ml TH | 1 | aggregates too large |
| 16 | P2-BT-100-2 | PFALTZ & BAUER C'IN | 40ml B+10ml TH | 2 | aggregates too large |
| 17 | P2-BT-100-3 | PFALTZ & BAUER C'IN | 40ml B+10ml TH | 3 | aggregates too large |
| 18 | P2-BT-100-4 | PFALTZ & BAUER C'IN | 40ml B+10ml TH | 4 | aggregates too large |
| 19 | P2-BT-100-5 | PFALTZ & BAUER C'IN | 40ml B+10ml TH | 5 | aggregates too large |
| 20 | S7-BT-200-1 | SIGMA C'IN C-3387 | 40ml B+10ml TH | 1 | aggregates too large |
| 21 | S7-BT-200-2 | SIGMA C'IN C-3387 | 40ml B+10ml TH | 2 | aggregates too large |
| 22 | S7-BT-200-3 | SIGMA C'IN C-3387 | 40ml B+10ml TH | 3 | aggregates too large |
| 23 | S7-BT-200-4 | SIGMA C'IN C-3387 | 40ml B+10ml TH | 4 | aggregates too large |
| 24 | S7-BT-200-5 | SIGMA C'IN C-3387 | 40ml B+10ml TH | 5 | aggregates too large |
| 25 | P2-BT-200-1 | PFALTZ & BAUER C'IN | 40ml B+10ml TH | 1 | aggregates too large |
| 26 | P2-BT-200-2 | PFALTZ & BAUER C'IN | 40ml B+10ml TH | 2 | aggregates too large |
| 27 | P2-BT-200-3 | PFALTZ & BAUER C'IN | 40ml B+10ml TH | 3 | aggregates too large |
| 28 | P2-BT-200-4 | PFALTZ & BAUER C'IN | 40ml B+10ml TH | 4 | aggregates too large |
| 29 | P2-BT-200-5 | PFALTZ & BAUER C'IN | 40ml B+10ml TH | 5 | aggregates too large |
| 30 | S2-BT-200-1 | SIGMA C'SAN C-0792 | 40ml B+10ml TH | 1 | |
| 31 | S2-BT-200-2 | SIGMA C'SAN C-0792 | 40ml B+10ml TH | 2 | |
| 32 | S2-BT-200-3 | SIGMA C'SAN C-0792 | 40ml B+10ml TH | 3 | |
| 33 | S2-BT-200-4 | SIGMA C'SAN C-0792 | 40ml B+10ml TH | 4 | |
| 34 | S2-BT-200-5 | SIGMA C'SAN C-0792 | 40ml B+10ml TH | 5 | |
| 35 | S6-BT-200-1 | SIGMA C'IN C-4666 | 40ml B+10ml TH | 1 | |

Samples in Table II can be identified as follows: 1-2-3-4:

1 Chitin or Chitosan Type.

S7=Sigma C-3387 Chitin
S6=Sigma C-4666 Chitin
P2=Pfaltz & Bauer CO-7632 Chitin
S2=Sigma C-0792 Chitosan
S0=Sigma M-3150 Methylglycol Chitosan

2 Paint Type and Additive.

B=Flat Black Rust-oleum 7776
G=Smoke Grey Rust-oleum 7786
T=5 ml Rust-oleum Thinner 7700
U=Ultrasound
EA=Ethyl Acetate

3 Particle Sizes.

-20=-20 + 45 Tyler Mesh
-45=-45 + 80 Tyler Mesh
-80=-80 + 100 Tyler Mesh
-100=-100 + 200 Tyler Mesh
-200=-200 Tyler Mesh

4 Dispersions.

1=1% by weight based on percentage paint non-volatiles
2=2% by weight based on percentage paint non-volatiles
3=3% by weight based on percentage paint non-volatiles
4=4% by weight based on percentage paint non-volatiles
5=5% by weight based on percentage paint non-volatiles

Preliminary Icephobic Tests

Five samples (-200 mesh Pfaltz and Bauer CO-7632 chitin dispersed in thinner, 1-5 wt. percent) and one control were placed in the freezer section (large pieces of ice--needed to be defrosted) of a small refrigerator for approximately four hours. Upon removal, all samples had a thin layer of ice over 10% of their surfaces.

After the freezer was defrosted, samples were dipped in a beaker of tap water and placed paint side up in the freezer at 0°C for 24 hours. Visual estimations showed:

| <u>Sample</u> | <u>% Ice on Painted Surface</u> |
|---------------|---------------------------------|
| Control-BT | 75% |
| P2-BT-200-1 | 40% |
| P2-BT-200-2 | 15% |
| P2-BT-200-3 | 30% |
| P2-BT-200-4 | 30% |
| P2-BT-200-5 | 40% |

RESULTS AND CONCLUSIONS

Of the five chitin/chitosan materials mixed with the Rust-oleum Flat Black polyurethane paint Tyler mesh screen fractions ranging from +20 to -200, in 1-5 wt%, the most successful dispersion, to date, appears to be the -200 mesh Pfaltz and Bauer C07632 chitin/paint thinner preblend system. Maceration techniques still require refinement. Dispersion has been aided by preblending the chitin/chitosan fractions with paint thinner but dispersion tests with seventeen other solvents proved unsuccessful. Further pre-blend work is required. Preliminary icephobic tests show the chitin coating system to be substantially better than standard paint in anti-icing properties. However, ice repulsion is not 100% at this time. More studies will be completed on chitin/chitosan types and percentages to aid in icephobic qualities.

REFERENCES

Burns, R. M and Beadley, W.W., Protective Coatings for Metals, 3rd. edition, American Chemical Society, New York, 1967.

Bogorodsky, V.V., Gavriilo, V.P. and Nedoshivin, O.A., Ice Destruction, D. Reidel Publishing Company, Dordrecht, Holland, 1983.

Characterization of Coatings: Physical Techniques Part II, ed. by Myers, R.R. and Long, J.S., Marcel Dekker Publishing, New York, 1976.

Chitin and Benzoylphenyl Ureas, ed. by J. E. Wright and A. Retnakaran, Dr. W. Junk Publishers, Series Entomoliga, Vol. 38, 1987.

Chitin in Nature and Technology, ed. by Muzzarelli, R., Jeuniaux, C. and Gooday, G., Plenum Press, New York, 1986.

Corrosion in Marine Environment, International Sourcebook I: Ship Painting and Corrosion, ed. by Deere, D.H., Hemisphere Publishing Corporation, A Halstad Press Book, John Wiley and Sons, Washington, 1977.

De Wolf, P., "Some New Considerations on the Testing of Antifouling Paints, 449-455, Biodeterioration of Materials, Halstad Press Division, John Wiley and Sons, New York, 1970.

Evans, D. M. and Levisohn, I., "Biodeterioration of Polyester-Based Polyurethanes", International Biodeterioration Bulletin, 4 (2), 89-92, 1968.

Fletcher, N.H., The Chemical Physics of Ice, University Press, Cambridge, Mass., 1970.

Hoffman, E. "The Development of Fungus-Resistance Paints," 370-375, Biodeterioration of Materials, Halstad Press Division, John Wiley and Sons, New York, 1970.

Ice and Snow: Properties, Processes, and Applications, ed. by Kingery, W. D., The M.I.T. Press, Cambridge, Mass., 1963.

Icing Problems and Recommended Solutions, ed. by Brun, E.A., North American Treaty Organization, Presented to the Flight Test Techniques and Instrumentation Panel of the Advisory Group for Aeronautical Research and Development (A.G.A.R.D.), November 1957.

Jones, E. B. G. and Irvine, J., "The Role of Marine Fungi in the Biodeterioration of Materials", Biodeterioration of Materials, Vol. 1, 1970.

Kaplan, A. M., Darby, R. T., Greenberger, M. and Rogers, M. R., "Microbial Deterioration of Polyurethane Systems," Developments in Industrial Microbiology, 9, pp. 201-217, 1968.

Microbiology of Extreme Environments and Its Potential for Biotechnology, ed. by M.S, DaCosta, J.C. Duarte and R.A.D. Williams, Elsevier Applied Science, London, 1989.

Muzzarelli, R.A.A., Chitin, Pergamon Press, Oxford, 1977.

Muzzarelli, R.A.A., Natural Chelating Polymers, Pergamon Press, Oxford, 1973.

Paint Additives: Developments Since 1977, ed. by Robinson, J.S., Noyes Data Corporation, Park Ridge, N.J., 1981.

Paint and Surface Coatings: Theory and Practice, ed. by R. Lambourne, Halstad Press: a division of John Wiley and Sons, 1987.

Paint Testing Manual: Physical and Chemical Examination of Paints, Varnishes, Lacquers and Colors, ed. by Sward, G.G., Thirteenth edition, ASTM Special Technical publication 500, American Society for Testing and Materials, Philadelphia, Pa., 1972.

Roberts, R.L. and Cabib. E., " *Serratia marcescens* Chitinase: One-Step Purification and Use for the Determination of Chitin," Analytical Biochemistry, 127, 404-412, 1982.

Ross, R. T., Sladen, J. B. and Wienert, L. A., "Biodeterioration of Paint and Paint Films," 330-338, Biodeterioration of Materials, Halstad Press Division, John Wiley and Sons, New York, 1970.

Royer, G. P., Fundamentals of Enzymology: Rate Enhancement, Specificity, Control and Applications, John Wiley and Sons, New York, 1982.

Schweitzer, P.A., ed., Corrosion and Corrosion Protection Handbook, Marcel Dekker Inc., New York, 1983.

Skinner, C. E., "Laboratory Test Methods for Biocidal Paints," 346-354, Biodeterioration of Materials, Halstad Press Division, John Wiley and Sons, New York, 1970.

Smith, R. N. and Goulding, K. H., "Primary and Secondary Evaluation of Microbiocides," 238-245, Biodeterioration of Materials, Halstad Press Division, John Wiley and Sons, New York, 1970.

APPENDIX I
LIST OF SUPPLIES

Pfaltz and Bauer, Waterbury CT 06708, (203) 575-0075:
Pfaltz and Bauer C07632 chitin.

Sigma Chemical Company, PO Box 14508, St. Louis, MO 63178, (314-771-5750):

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

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%.

DESOTO Inc., Chicago Heights, IL, (312)-391-9000:

Desoto Super Desothane Aliphatic Polyurethane Enamel paint
(36270)

Desoto Activator MHS-420

Desoto Mil T-81772A thinner.

Rust-oleum Corporation, 11 Hawthorn Pkwy, Vernon Hills, Ill.
60061 paints:

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

Aluminum (8 mm--3003H14):Bralco Aluminum Co., 8321 Cansord,
Pico Rivera, CA 90660, (213) 588-0161

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

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

AR HCl: A144-212, lot #897062
Fisher Scientific Inc., Fair Lawn, N.J. 07410

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

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 VXK
Mallinckrodt Chemical Works, St. Louis, MO 63160

formaldehyde: 5016-500, Lot 4456 KCV
Mallinckrodt Chemical Works, St. Louis, MO 63160

formamide: FX0420-3, Lot 7076
EM Science, 111 Woodcrest Rd., Cherry Hill, NJ 08034

glycerol (1:1 with H₂O): BP-229-1000, Lot 881437
Fisher Scientific Inc., Fair Lawn, N.J. 07410

hexanes: HXo310-1, Lot 8022
EM Science, 111 Woodcrest Rd., Cherry Hill, NJ 08034

methyl isobutyl ketone: M-213, Lot Z40183
Fisher Scientific Inc., Fair Lawn, N.J. 07410

methylene chloride: D-150, Lot 857070
Fisher Scientific Inc., Fair Lawn, N.J. 07410

methylsulfoxide: 22680, Lot 09231 JW
Aldrich Chemical Co., Inc., Milwaukee, KK 53233

Spirits of Turpentine (steam distilled) 330522:
Power Kleen Solvents, Inc. Wheeling, Ill. 60090.

toluene: T324-4, Lot 893972
Fisher Scientific Inc., Fair Lawn, N.J. 07410

xylenes: XX0055-1, Lot 8245
EM Science, 111 Woodcrest Rd., Cherry Hill, NJ 08034

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