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WATERBORNE POLYURETHANE BINDER RESINS FOR COMPLIANT AIRCRAFT COATINGS

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This Small Business Innovation Research (SBIR), Phase I research project investigated the feasibility of producing a one-component, water-borne, low volatile organic compounds (VOC) coating for the protection of naval aircraft and ground support equipment. Novel silane-terminated, silicone-modified, polyurethane copolymers were prepared and evaluated.

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FINAL REPORT

Waterborne Polyurethane Binder Resins for Compliant Aircraft Coatings

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Francis L. Keohan, Regina M. Stewart,
and Wendy M. Gomes

TECHNICAL SUMMARY

This six month Phase I research project has investigated the feasibility of producing a one-component, water-borne, low volatile organic compound coating for the protection of naval aircraft and ground equipment. Novel silane-terminated silicone-modified polyurethane copolymers have been prepared. These copolymers, when mixed with a silicate crosslinker and water produced hard, fast-curing, adherent coatings on aluminum panels. These coatings were tested for curing and drying times, adhesion, pencil hardness, and color retention. More extensive testing will be reserved for the Phase II program. Several formulations did quite well in the tests that were performed. The results suggest that a Phase II program should be undertaken to fully evaluate and formulate an effective one-component, low-VOC coating for the protection of naval aircraft and ground vehicles.

POTENTIAL APPLICATIONS

EPA regulations regarding the volatile organic compound content of coatings are becoming more stringent. Outside of the need for protective coatings for naval aircraft and other vehicles, there are a number of potential applications for one-component, low volatile organic compound coatings. These new coatings could potentially be used for architectural and industrial coatings. Not only are these coatings better for the environment, they are also safer to manufacture and to apply. In addition, substantial cost savings are possible through reducing the amount of solvent or replacing organic solvents with water.

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1.0 PHASE I RESEARCH OBJECTIVE

The objective of this Phase I research program was to establish the feasibility of preparing a water-borne, low volatile organic compound (VOC), one-component binder system for Navy use which would provide a rapid cure to a tough adherent film which would withstand the demanding environment imposed on naval aircraft and ground vehicles. Reducing the VOC content to meet the present EPA regulations while still maintaining the same level of protection that is presently achieved using conventional coatings was a major aspect of this Phase I.

The coatings that are now used by the Navy for the protection of aircraft, ground vehicles, and other pieces of equipment are prepared with large amounts of volatile solvents. Due to the EPA's increasingly restrictive rules regulating the amounts and kinds of solvents allowed, there has been a tremendous surge of interest in the area of low VOC coatings. It is expected that by 1995, the U. S. market for more environmentally acceptable coatings will grow rapidly, while the market for certain coatings like low-solids and high-solvent systems will fall from 44% to 26%.[1] In addition, the majority of the coatings now used are two-component, which requires that they be mixed and used within a short period of time.

2.0 BACKGROUND

Due to the increasingly restrictive guidelines emanating from the Environmental Protection Agency concerning the volatile organic compound (VOC) content of coatings, research into low solvent coating technology is on the increase. At this time, there are five major types of low VOC coatings: powder coatings, high-solids coatings, UV-curable coatings, exempt solvent coatings, and water-borne coatings. In this program the entire focus was on water-borne coatings.

There are many advantages associated with the use of water-borne coatings. Much of the same equipment that is used to prepare and apply conventional coatings can be used for water-borne coatings. Using water makes clean-up much easier, relieves much of the odor problem that accompanies the use of large quantities of organic solvents, decreases the fire hazard, and reduces solvent emissions. As with the other low-VOC coating technologies, there are also disadvantages such as increased drying times due to the lower volatility of water compared to organic solvents (but the surface can be smoother upon drying), poor solvent and flow characteristics, poor freeze/thaw stability, limited shelf stability, and poor detergent resistance.[2] In addition, for some systems, strict humidity control during application and pretreatments of the substrate surface are often needed.

One of the major causes for paint failure is extended exposure to weather and operational chemicals which embrittle and discolor the coating, causing paint around fasteners and seams to crack and chip, thus exposing bare metal.[3] U. S. Naval aircraft are subject to one of the most corrosive natural environments known, since they are normally deployed within close proximity to salt water and high humidity.

Aliphatic polyurethane resins have become the predominant technology for military aircraft coatings due to their durability and flexibility. Their application, however, frequently requires significant dilution with volatile solvents. The standard organic coating system applied to Navy aircraft consists of an epoxy primer and a polyurethane topcoat. The pigment in this primer, strontium chromate, is well known as an exceptional corrosion inhibitor, especially for aluminum.[4] Due to its exceptional adhesion, corrosion inhibition, and durability, this system has been used to protect aluminum aircraft structures from the harsh environment in which they operate. The lifetime of this primer and topcoat system on Navy aircraft is four to six years, after which the coating must be chemically or physically removed.

The proposed research explores the feasibility of chemically modifying a conventional polyurethane resin for water dispersion and cure via a unique crosslinking mechanism. The benefits include lower product toxicity and savings from the elimination of costly solvents.

The system being studied involves the use of silicate glass precursors and alkoxysilane functionalized organic polymers to produce unique hybrid structures in the presence of water. Sol-gel technology involves the condensation polymerization of tetrafunctional silicate monomers to produce dense, water- and carbon-free "glasses" at low temperatures.[5] In these reactions, the silicate monomers, $Si(OR)_4$, react with water to produce silanols ($Si(OR)_3OH$). These silanols then react with other silanols or with an alkoxide group to produce a siloxane (Si-O-Si) linkage. Usually, these reactions are carried out in a solvent because the silicates are not miscible with water. Due to the complexity of this system, it is difficult to determine the extent of polymerization. Partially hydrolyzed and partially condensed species are likely. In addition, the reaction is pH sensitive. The resultant polymers should be hard, durable, and thermally resistant. The low temperature chemical processing of these polymers makes them suitable for use as protective coatings.

The polyurethane backbone should impart flexibility, toughness, and a strong affinity for polar substrates. The trialkoxysilane endcaps on the polyurethane molecules are designed for condensation crosslinking reactions with tetraethylorthosilicate in order to achieve the durability and adhesion of the solvent-borne polyurethane based paints currently used by the Navy. In the experimental polymers, the silicone blocks were used to improve the low temperature flexibility as well as for their outstanding surfactant properties.

3.0 PHASE I RESEARCH

The main objective of this Phase I project was to identify and prepare a one-component, low-VOC coating which the Navy could use for aircraft as well as ground vehicles. To do this, it was necessary to show, through laboratory experiments, the feasibility of synthesizing novel siloxane-modified polyurethane copolymers, formulating them into water-borne paints and testing the performance of the resulting coatings.

Since a Phase I constitutes a feasibility study, it was important to establish that the basic chemistry involved in the preparation of the graft copolymers and the formulations of the coatings could be developed to the point where an expanded Phase II R and D program would result in a low-VOC, one-component coating formulation for naval aircraft which would work as well, if not better, than the presently used solvent-based coatings. This technology would also be applicable to a wide range of military coating problems where VOC emissions must be minimized. Specialty maintenance coatings for many Naval applications could be developed using this binder system.

3.1 Proposed Research and Experimental Program

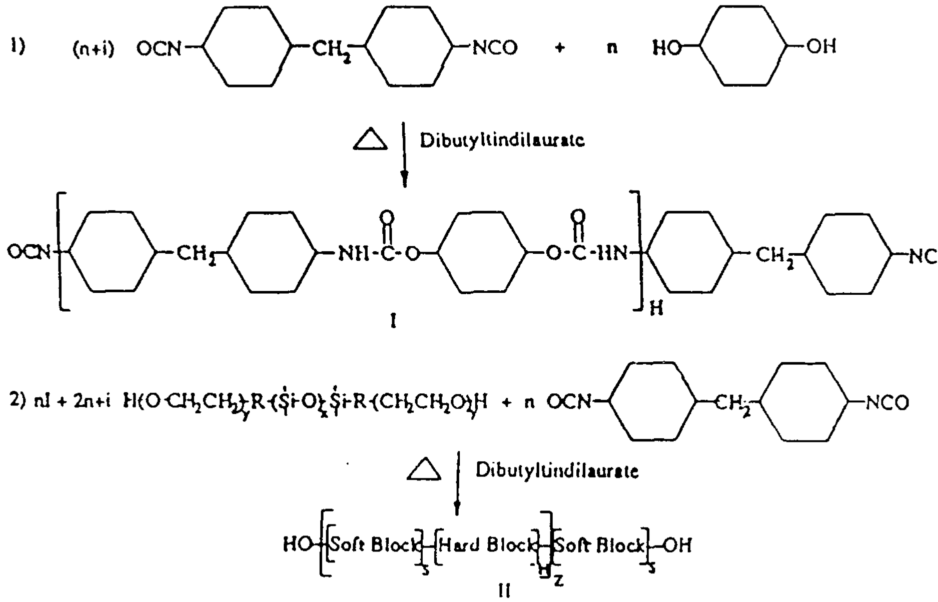
Proposed Research

To address the needs of Naval aircraft repair operations, the focus of the Phase I research was directed at formulating a single-package, low VOC topcoat which could be applied by brush or spray. In order to accommodate these changes from the solicitation, major changes were made in the experimental approach as well as the testing of the final products. These tests are discussed more fully in Section 3.6.

Experimental Program

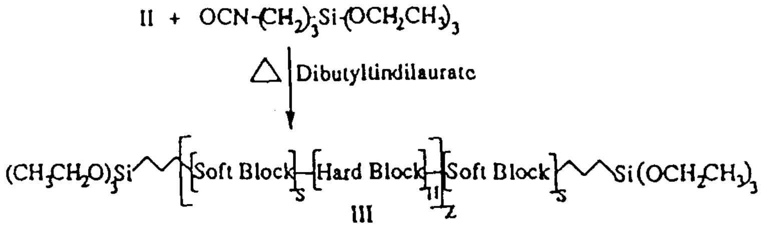
The original idea for a two-component anti-corrosive coating involved preparing trialkoxysilane-terminated poly(silicone-urethane) copolymers and formulating them into water-reduced paints. This research was based on the premise that the combination of silicone-polyethylene oxide soft blocks in an aliphatic polyurethane backbone followed by a sol-gel crosslinking technique would provide the necessary water dispersibility, adhesion, and barrier properties required for this application. Although the original concept was not geared toward preparing a one-component coating, it was hoped that some portion of the chemistry could be altered to accommodate this new aspect of the problem.

A cycloaliphatic diisocyanate (methylene bis (4-isocyanato cyclohexane) Desmodur W) and a cycloaliphatic diol (1,4-cyclohexane diol) were reacted in a 1.5:1 molar ratio with heat for 45 minutes. Then a polyethyleneoxide polydimethylsiloxane (PS-555) was added, both with and without heat. This siloxane has an average molecular weight of 2400 g/mole and is 45-55% polyethylene oxide.

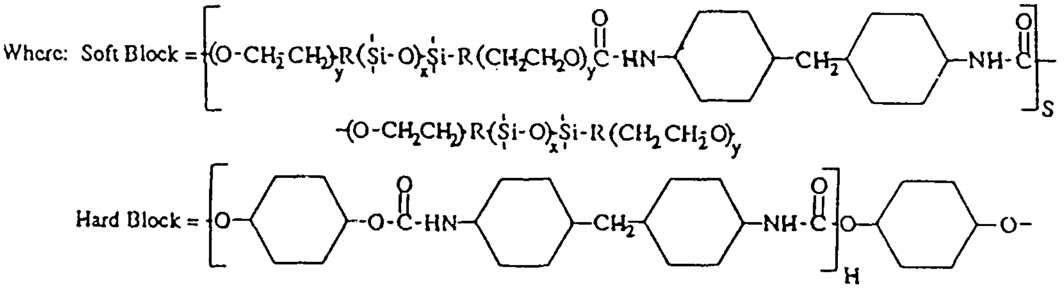


After 45-60 minutes, 3-isocyanatopropyltriethoxysilane was added and the solution was stirred for at least 24 hours. The product of this reaction, a silane-terminated polymer, was used to prepare several coatings. Coatings prepared using these polymers were formulated with propylene glycol methyl ether acetate (PGMEA), para-toluene sulfonic acid, Desonic 12N, tetraethylorthosilicate (TEOS), and water. Unfortunately, these formulations needed heat to cure. In addition, these polymers frequently precipitated or gelled upon standing.

3)



4) III + $Si(OCH_2CH_3)_4$ + $H_2O \longrightarrow$ Crosslinked Polyurethane-Silicate Ceramer



The next step was to prepare an uncapped polymer (no prior reaction with the alkoxysilane). It was thought that perhaps the crosslinking reaction would proceed more quickly if the alkoxysilane were partially reacted with the TEOS prior to the addition to the siloxane portion of the formulation. The polymer and the catalyst (p-toluene sulfonic acid) were mixed with solutions of the silane and TEOS. Water was added afterwards. Once again, these formulations needed heat to start the crosslinking reaction.

It seemed reasonable to expect that a stronger catalyst would increase the cure rate, thereby eliminating the need for heat curing. For several coating formulations, the p-toluene sulfonic acid was replaced with a 10% nitric acid solution as catalyst. Unfortunately, the coatings prepared using the nitric acid catalyst were very brittle. Within 24 hours, all of them had crumbled. Varying the amount of nitric acid solution used made little difference in the final coating formulations.

Due to the problems encountered with the stability of these experimental polymers, new polymers were prepared. For these new polymers, the cycloaliphatic diol was left out of the reaction, and the isocyanatoalkoxysilane was replaced with an aminoalkoxy silane. (These reactions are discussed in detail in Sections 3.2 and 3.3.) These new experimental polymers were highly viscous liquids which did not gel like those prepared with the cyclohexane diol. Coatings prepared from these polymers dried to smooth, uniform films but failed to develop sufficient hardness, even after one week.

In order to circumvent these solubility and curing problems, it was decided to try to modify several commercially available polyurethanes as the basis for the coatings. Hexcel Uralite 3140 (Part A) was used even though it is an aromatic polyurethane and part of a two-component system, because the part A component consisted of a well-defined, isocyanato-terminated hard-soft block system. This material, while basically unusable as an aircraft topcoat binder because of its aromatic character, served as an effective model compound for the desired aliphatic polyurethane backbone. The Hexcel was reacted with an alkoxysilane (N-methylamino propyltrimethoxy silane) for 30 minutes (until the isocyanate band had disappeared from the IR spectrum). TEOS, p-toluene sulfonic acid,and water were added. The coatings formed not only dried to smooth, uniform films, they cured in the required time (<8 hours). Unfortunately, when these samples were placed in the oven at 350°F, they turned very brown. (Probably because of the aromatio portion of the polyurethane.)

Next, coatings were prepared using mixtures of the new trialkoxysilane-capped PS-555 Hexcel 3140 polymer solutions. It was hoped that the Hexcel 3140 would increase the hardness, while the PS-555 polymer would increase the solution's miscibility and prevent it from cracking upon curing. The coating samples that were prepared all looked good until the yellowing test. The major problem encountered so far had been the yellowing of the coating in the oven test. Even samples with a small amount of the Hexcel Uralite 3140 turned quite yellow during the oven test. It is believed that the aromatic portion of the polyurethane was the most likely reason for the dark yellow color. Finding an aliphatic polyurethane with other properites similar to those of Hexcel Uralite 3140 was important.

A low-viscosity aliphatic polyurethane from Quinn and Company called QThane QC 4559 was chosen on this basis. This QThane QC 4559 is a low viscosity, 90% solids, aliphatic polyurethane. The coatings prepared from the trialkoxysilane-capped derivate of QC 4559 were very hard, looked nice and did not discolor too badly, but did not cure in the required time. In addition, the aqueous dispersion did not stay mixed well. The two surfactants that were tried Desonic 12N and Surfynol 104H, made no visible difference in the miscibility of these solutions.

Next, it was decided to try different polysilicates in place of TEOS. PS-9125 and PS-9150, which are polyalkoxysiloxane-polysilicates, are often used in sol-gel applications. Therefore, the TEOS was replaced with PS-9125 (polydiethoxysiloxane) and PS-9150 (diethoxysiloxane/diethoxytitanoxane) in several reactions to see if these silicates (titanates) would have an effect on the curing rate or the final hardness of the coatings. For the formulations prepared with PS-9125, the coatings were hard and rubbery. With PS-9150, the formulation started to gel and turn brown before any coating was prepared. These same reactions were repeated with less catalyst and nice coatings were prepared, but they yellowed badly, especially the one prepared with PS-9150, possibly due to the titanium. (Titanium alkoxides are known to catalyze the condensation of silanols to siloxanes.)

Tetramethylorthosilicate (TMOS) and tetrabutylorthosilicate (TBOS) were also tried in the place of TEOS. The coating prepared with TMOS was very smooth, but it cracked in several places, while the formulation prepared with TBOS suffered severe miscibility problems and would not cure.

Acidified Montmorillonite clays have also been used as the catalyst in these reactions. There have formed some very strong coatings, but they either take too long to cure or they yellow badly in the oven after a short time. In order to increase the cure rate the catalyst was changed to an 85% solution of phosphoric acid. This catalyst increased the cure rate too much, so a dilute acid solution was prepared (10% solution of 85% phosphoric acid). Solid phosphoric acid, which should not react with anything until the water is added, has also been used and some very nice looking coatings have been prepared.

In addition to the other problems encountered with the different catalysts that were tried, there is the problem of pH dependence of sol-gel condensation reactions. The rates of the hydrolysis and condensation reactions are dependent on solution pH, the water concentration, and the alkoxide used. The pH has the strongest effect of the three. The hydrolysis reaction is catalyzed by both acids and bases, but the condensation reaction is fastest at a pH about 5-6.[6] Increasing the acid catalyst used will obviously lower the pH and could therefore slow the reaction.

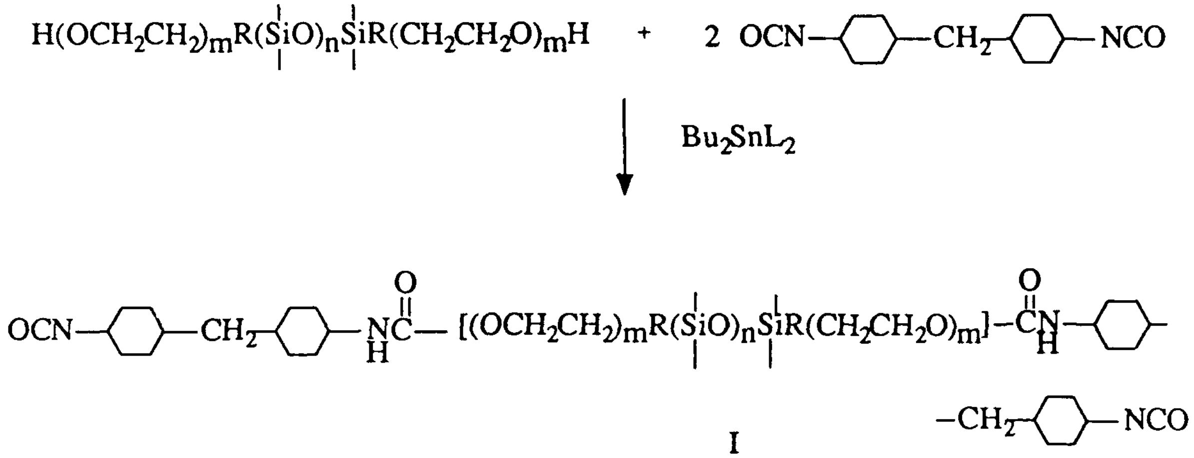
As stated earlier, the worst problem we have encountered has been yellowing of the coating after one hour at 350 °F. If there were a small amount of unreacted isocyanate or unreacted amine present, then these would contribute to the color change. To test this hypothesis, reactions were done in which the aminosilane endcapping agent was replaced in whole or in part with a mercaptosilane or methanol. For the coatings prepared from formulations using the mercaptosilane, there was less of a color change, but the coatings did not cure. For the coatings prepared with methanol, there was no visible change in the cure rate or the color change.

A multitude of different coatings have been prepared, but the most promising coatings were formulated with a combination of an aliphatic polyurethane (QThane QC 4559) and a siloxane/polyurethane copolymer which had been reacted with an aminosilane. When these components were mixed with TEOS, a catalyst, and water, a reaction commenced which led to a crosslinked, tough, durable film. Several of these coatings were studied in more detail and those results follow. The most important aspect of this coating system is that until water is added, immediately prior to its use, it is stable. There will be a minimum amount of water needed to form tough, fast-curing coatings, but after that more water can be added to dilute the paint for different types of applications. The upper limit of aqueous dilution which can be tolerated has not, as yet, been determined.

3.2 Synthesis of Silicone-Modified Polyurethane Resins

The initial step in the preparation of the copolymers was to prepare the silicone-modified polyurethane polymers. These polymers are the key to the coating system because they should impart the desired properties of water compatibility in the uncured state and outstanding adhesion to metallic substrates and durability in a marine environment in the cured state to the final graft copolymers.

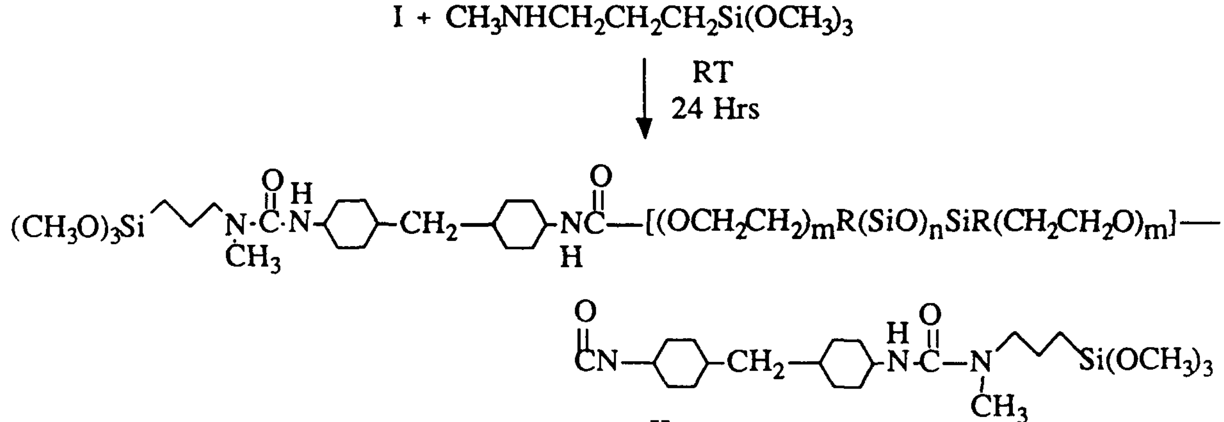
A carbinol-terminated dimethylsiloxane/ethylene oxide block copolymer was chosen to introduce silicone and hydrophylic groups into the resins. The copolymer PS-555 has a molecular weight of 2400 and a polyethylene oxide content of 50 percent by weight. This siloxane was reacted with methylene-bis (4-isocyanatocyclohexane) (in a 1:2 ratio) in the presence of dibutyltin dilaurate to produce an isocyanate-terminated polymer.



I

3.3 Synthesis of Silane-Terminated Polyurethane Copolymers

In the next step of the synthesis the isocyanate-functional silicone/urethane block copolymer (I) was further reacted with N-methylaminopropyl trimethoxy silane (in a 1:2 ratio) to produce a silane-terminated polymer (II).



II

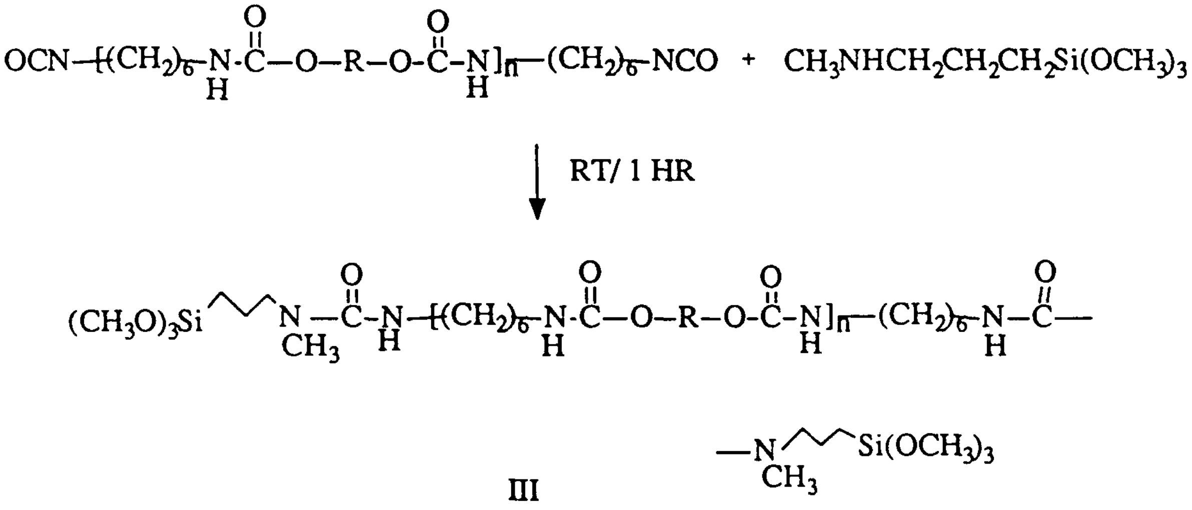
If THF was used in this reaction, then it was removed by trap- to- trap distillation afterwards to leave a very viscous oil. Propylene glycol methyl ether actetate (PGMEA) was then added to this mixture.

This polymer solution was then used as is (solution in PGMEA) for formulation of the coatings. (These reactions were followed by IR spectroscopy. For the first step of the reaction, the disappearance of the OH band indicated that the reaction was complete. For the second step of the reaction, the disappearance of the isocyanate band indicated that the reaction was complete.)

Originally, the plan was to prepare coatings using polymers prepared from PS-555, but coatings prepared in this manner did not cure to a hard coating in the required time. So a modified aliphatic polyurethane was added to the system to increase the hardness.

3.4 Synthesis of Modified Polyurethane

Quinn QThane QC 4559 is a high-solid, low viscosity (350 cps) polyurethane which is typically one part of a two-component coating. The Quinn QC 4559 was reacted with the N-methylaminopropyltrimethoxysilane to produce a silane-terminated polyurethane. Propylene glycol methyl ether actetate was then added to this solution, which was used to prepare coatings.



$$OCN{-}[(CH_2)_6{-}\underset{H}{N}{-}\overset{O}{\overset{\|}{C}}{-}O{-}R{-}O{-}\overset{O}{\overset{\|}{C}}{-}\underset{H}{N}]_n{-}(CH_2)_6{-}NCO + CH_3NHCH_2CH_2CH_2Si(OCH_3)_3$$

$$\big\downarrow \text{RT/ 1 HR}$$

$$(CH_3O)_3SiCH_2CH_2CH_2\underset{CH_3}{N}{-}\overset{O}{\overset{\|}{C}}{-}\underset{H}{N}{-}[(CH_2)_6{-}\underset{H}{N}{-}\overset{O}{\overset{\|}{C}}{-}O{-}R{-}O{-}\overset{O}{\overset{\|}{C}}{-}\underset{H}{N}]_n{-}(CH_2)_6{-}\underset{H}{N}{-}\overset{O}{\overset{\|}{C}}{-}\underset{CH_3}{N}CH_2CH_2CH_2Si(OCH_3)_3$$

III

3.5 Preparation of Coatings

The main components of these coatings are the low molecular weight aliphatic polyurethane resin (Quinn QC 4559), tetraethylorthosilicate, our silane-terminated experimental copolymers, and water. When these components were mixed together and applied to aluminum panels, these formulations dried into tough, adherent films.

$$\text{II} + \text{III} + Si(OCH_2CH_3)_4 + H_2O \longrightarrow \text{Crosslinked Polyurethane Silicate Ceramer}$$

The PS-555/silane/PGMEA solution (Part A) and the Quinn/silane/PGMEA solution (Part B) were mixed together in varying ratios with high speed stirring for at least 30 minutes. Then the tetraethylorthosilicate (in a ratio of 85:15 of Part A and Part B (excluding solvent): SiO_2) and the titanium dioxide (33 wt % of solids) were added to the mixture with high speed stirring. (The titanium had been ground in a ball-mill for 2-3 hours prior to its addition.) After this solution had been stirred for 30 minutes, the catalyst, a 10% solution of 85% phosphoric acid, was added to the formulation. Although, this catalyst is a water solution, it is used in such small amounts that the water content has not caused a problem with the shelf life of the paint. (Solid phosphoric acid has also been used as the catalyst in these reactions and would continue to be used in the Phase II.) After 15 minutes, deionized water was added to the solution. Usually within several minutes there was a noticeable increase in the viscosity of the solution. After mixing thoroughly, the solution was either poured into aluminum pans or sprayed onto aluminum panels.

Each solution was poured into two aluminum dishes and allowed to dry overnight before being evaluated. The coatings were usually dry to the touch in 1-3 hours and completely dry within 24 hours. For those samples which looked good after 24 hours, they were then placed in a 350 °F oven for one hour. If these samples did not yellow badly, these formulations were sprayed onto aluminum panels that had been solvent degreased, abraded with a paste of Alconox detergent and water, etched with Pasajell 105 (a gelled acidic etch for aluminum alloys), and primed with an aircraft epoxy polyamide primer MIL-P-23377E. The panels were allowed to cure for one week prior to any testing of the samples.

There was a very careful balance of the curing rate and hardness. The Quinn QC 4559 gave the added hardness that was needed for our coatings, while the PS-555 lowered the rate of curing of the mixture and greatly improved the miscibility of the components. The trialkoxy silane-capped Quinn, by itself, would not form a miscible solution with tetraethylorthosilicate and water. When samples were poured from this solution into aluminum pans, the TEOS and water formed a layer on top of the remainder of the solution. When the TEOS and water had evaporated, a very hard, brittle coating remained. Coatings prepared with PS-555 by itself would not form hard coatings.

The criteria used to judge the different coating formulations prepared included ease and thoroughness of mixing, pot-life, drying time, pencil hardness, wet adhesion, and color and gloss retention at 350 °F. The most difficult portion of this project has been trying to produce a one-component paint which dries to the touch in 2 hours yet has a 2-4 hour potlife and a one year shelflife.

The main problems encountered so far are discoloration upon heating and shorter pot and shelf lives then desired. The Phase II would concentrate on solving these problems and identifying other possible coating formulations perhaps through altering the PS-555 or finding a different commercially available polyurethane.

3.6 Testing of Coating Formulations

The coatings were subjected to a variety of tests, which included drying times (ASTM D 1640), pencil hardness (ASTM D 3363), yellowing test (ASTM D 2244), wet adhesion (MIL-L-81352A), and a MEK rub test (MIL-C-85285B). The best way to achieve an effective barrier to water vapor transmission and to have low permeability to small molecules is to apply multiple layers of a coating. This aids in sealing off pores and covering other film defects. Better results are expected for multiple layers of coatings. For this reason, two coats were applied to each panel several days apart. The following table gives the results of these above mentioned tests for the three samples which were sent to NADC for evaluation.

#	Quinn:PS -555	Tack Free	Dry Hard	Pencil Hardness	Wet Adhesion	350 °F	MEK Rub Test
RMS-I-129	1:1	2 hrs	8 hrs	4	no delamination	light yellow	nothing removed
RMS-I-127	2:1	2 hrs	10 hrs	5	partial delamination	light yellow	nothing removed
RMS-I-128	1:2	2 hrs	8 hrs	3	delamination of one coat	dark yellow	much removed

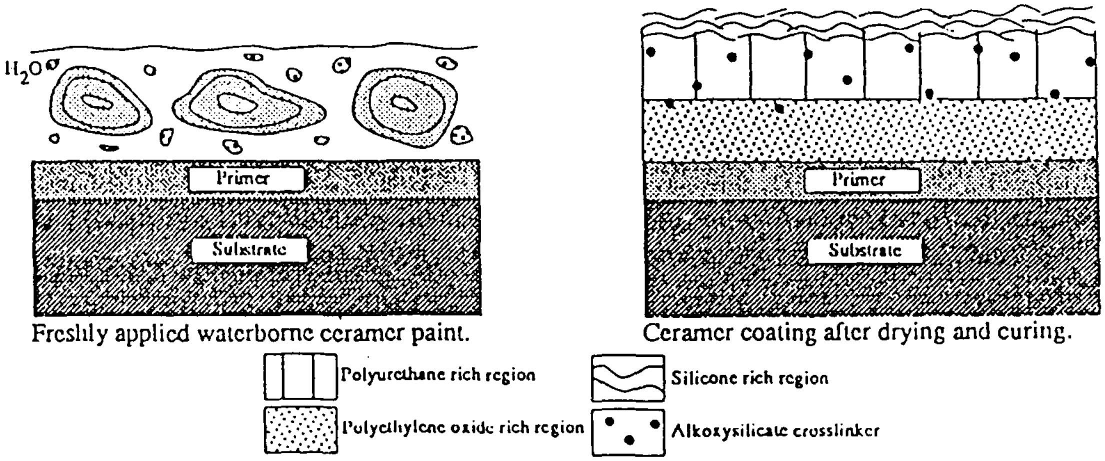
Of the three coating formulations that were sprayed onto primed 2024-T3 aluminum panels for further testing, the one prepared with a 1:1 ratio of the PS-555 polymer solution to the Quinn solution performed the best. There was no delamination from the wet adhesion test or the MEK rub test and the coating yellowed only slightly after one hour at 350 °F. The coating which performed the worst was the one with a 2:1 ratio of the PS-555 solution to the Quinn solution. In the wet adhesion test, almost one entire coat was delaminated. In the MEK rub test, much of one coating was removed and in the yellowing test, the coating turned a dark yellow. The delamination during the adhesion and MEK tests was most likely due to the increased amount of polyethylene oxide (or soft blocks) in the formulation. This makes the coating more susceptible to water and polar solvents. The coating prepared with a 1:2 ratio of PS-555 to Quinn took a little longer to dry hard than the others and there was a little delamination from the wet adhesion test. The results of the other tests were quite good. Photographs of the panels after the wet adhesion tests are shown in Appendix I.

Tensile Tests

Attempts to prepare thin film samples and molds of several coating formulations, were, by and large, unsuccessful. Very thin films were too difficult to handle and thick films did not cure evenly since the formulations cured quickly. Several samples were tested for tensile strength using a Universal testing machine. The cast dogbone specimens were brittle, notch sensitive, and difficult to measure in cross section due to solvent drying effects. The average of seven samples was 1200 ± 200 psi with a percent elongation of 5%.

Contact Angle Measurements

The basis for this experimental approach has been that the unique structure and composition of the block copolymers will impart water compatibility when uncured and dispersed in a water base and hydrophobicity and effective barrier properites when cured to a film. The key to this behavior is the dual role of the PS-555 polymers. In the uncured state, polyethylene oxide (PEO) segments should orient themselves toward the aqueous dispersion medium, thus aiding the stability of the paint. Upon curing the hydrophilic PEO portions would tend to associate with the polar substrate while the strongly hydrophobic polysiloxanes would migrate to the coating-air interface. With this orientation, the coating would exhibit maximum barrier properties and water resistance. An illustration of this coating concept is shown below. This could possibly cause intercoat adhesion problems if additional coats were not applied soon after the first coat.



Freshly applied waterborne ceramer paint.

Ceramer coating after drying and curing.

Using a Gaertner Scientific goniometer, the contact angles of the three panels coated with the three formulations sent to NADC for testing were measured. In addition, the contact angles of both the air-coating interface and the aluminum-coating interface of two other samples were measured. The results are shown in the following table.

Effect of Coating Compositon and Orientation on Water Contact Angle

#	Air-Coating Interface	Aluminum-Coating Interface	Q-Thane/PS-555 Ratio
RMS-I-127	61	--	2 : 1
RMS-I-129	54	--	1 : 1
RMS-I-128	28	--	1 : 2
Teflon	68	--	--
Glass	56	--	--
WG-II-172	69	63.5	1 : 1
WG-28-162	72.5	57.5	2.5 : 1

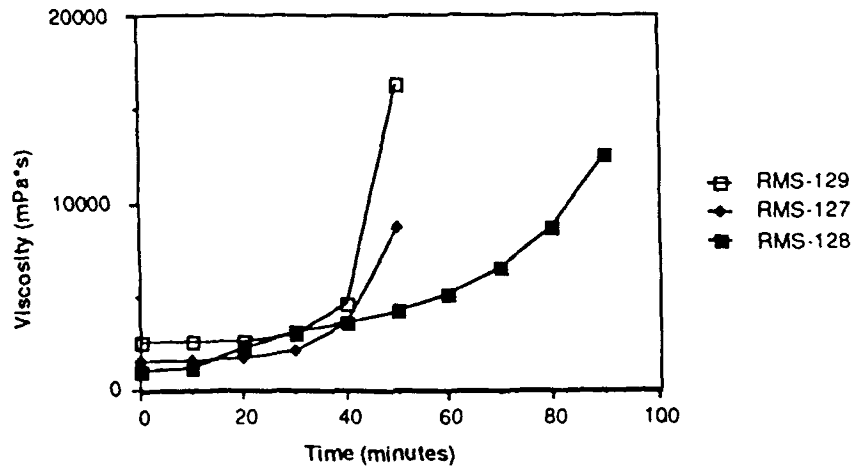
The contact angles for both teflon and glass are shown in the table. Teflon, as a highly hydrophobic substrate has a contact angle of 68, while glass has a contact angle of 56. RMS-I-128, which has the most PS-555 in it, and therefore the most PEO, has the smallest contact angle and therefore the best wettability. RMS-I-127, which has the least PS-555 and therefore the least PEO, has one of the largest contact angles and therefore worse wettability. The formulation which performed the best overall was RMS-I-129 and its contact angle of 54 is not much greater than that of RMS-I-127.

For the last two samples in the table, WG-II-172 and WG-28-162, the contact angles of each side of the coatings were measured. WG-II-172 was prepared with a 1:1 ratio of the Quinn polymer:PS-555 polymer. WG-28-162 was prepared with a 2.5:1 ratio of the Quinn polymer:PS-555 polymer. Samples were poured into aluminum pans. When the samples had dried they were removed from the pans and the contact angle of each side of each coating was measured. For both samples the contact angle at the air-coating interface is larger than the contact angle at the aluminum coating interface which supports the idea that the polyethylene oxide segments and the silicone segments migrate in opposite directions upon curing.

Viscosity Measurements

Viscosity measurements were made using a Brookfield Model LVT Rotary Viscometer at room temperature. Measurements were taken every ten minutes to see how the viscosity changed over time. The graph below shows the results of these viscosity measurements.

Viscosity Development in Waterborne Polyurethane-Silicate Formulations



As the graph shows, RMS-I-129, which performed the best in the other tests, increased very rapidly in viscosity in the first hour. RMS-I-127 increased in viscosity less rapidly, while the viscosity increase of RMS-I-128, which performed the worst in the other tests, was much more gradual.

3.7 Experimental-Syntheses of Copolymers

The intermediate silicone-modified polyurethane resins and the final graft copolymers were characterized by Fourier Transform Spectroscopy (FTIR) as described in Section 3.8. Several FTIR spectra are found under their assigned figure numbers in the Appendix II.

The polydimethyl/ethylene oxide siloxanes and the N-methylaminopropyltrimethoxysilane were purchased from Huls America, Bristol, PA. The Quinn QC 4559 was generously supplied by Quinn and Co, Seabrook, NH. Hexcel Uralite was purchased from Chembar, Inc., Groveport, OH. The Surfynol 104 H was generously supplied by Air Products, Allentown, PA. The Desonic 12N was generously supplied by De Soto, Inc. Desmodur W was generously supplied by Mobay Corp, Pittsburgh, PA. The Pasajell 105 was generously supplied by SEMCO, Glendale, CA. The epoxy primer was made according to the specification MIL-P-23377E and was purchased from New England Paint Mfg. Co. Inc., Central Falls, RI. All remaining chemicals were purchased from Aldrich Chemical Company, Milwaukee, WI.

All glassware was oven-dried at 120 °C to remove all traces of water. Water was removed from the siloxane by azeotroping it with toluene.

Synthesis of Silane-Terminated Polydimethylsiloxane Copolymer (Part A)

PS-555 (10.066 g, 3.770 mmol),methylene-bis-(4-isocyanatocyclohexane) (1.96 g, 7.48 mmol), and dibutyltin dilaurate (0.120 g, 0.190 mmol) were added to a three-necked round bottomed flask equipped with a stir-bar, a gas inlet attached to a nitrogen tank, and two septum (a rubber membrane to prevent water contamination of polymers). Propylene glycol methyl ether acetate (PGMEA) (5.2 g) was added to the reaction. The reaction mixture was stirred overnight. An IR spectrum taken after 16 hours showed that the majority of the OH band had disappeared. Then N-methylaminopropyltrimethoxysilane (1.24 g, 6.415 mmol) was added to the reaction mixture by syringe. After one hour an IR spectrum showed that all of the isocyanate had reacted. This solution was then used as is for preparing the coatings.

Synthesis of Silane-terminated Polyurethane (Part B)

Quinn QC 4559 (10.091 g, 19.864 mmol), N-methylamino propyl trimethoxysilane (7.679 g, 39.73 mmol), and propylene glycol methyl ether acetate (7.616 g) were added to a 100 mL three-necked round-bottomed flask. The reaction mixture was stirred for one hour. An IR spectrum of the solution showed that the isocyanate band had disappeared. This solution was then used as is for preparing the coatings.

Both reactions were repeated numerous times.

3.8 Analytical

Infrared Spectroscopy was performed on a Perkin-Elmer Model 1600. Samples were thin films cast on to KBr windows. In general, 16 scans were taken of each sample. (See AppendixII.) The silicone-modified polyurethane reactions were followed by the disappearance of the absorption between 3400-3200 cm^{-1} in the IR spectrum from the OH endgroups (FIGURE I). The graft polymerization reactions were followed by disappearance of the absorption at 2200 cm^{-1} in the FTIR spectrum from the free isocyanate (FIGURE II).

The theoretical VOC content of the coatings was calculated. It was assumed that all of the TEOS would react with water to produce ethanol.

$$Si(OCH_2CH_3)_4 + 2H_2O \longrightarrow SiO_2 + 4CH_3CH_2OH$$

It is extremely unlikely that for every molecule of TEOS used, four molecules of ethanol are produced; but for our purposes, these calculations determined what the maximum VOC content of these coatings would be. The calculation came out to be 344g/L.

In addition, tests were run on several samples to determine the percent volatiles in the experimental formulations (ASTM D 2369). As this test was run immediately after the paint formulation was mixed, no time was allowed for the water to react with the TEOS. For this reason, the 51-53 % volatile values are probably a little high.

4.0 CONCLUSIONS & TECHNICAL FEASIBILITY ESTIMATE

This Phase I research program has demonstrated the feasibility of preparing a low-VOC, one-component, water-borne silicone-modified polyurethane coating for the protection and repair of airplanes and ground vehicles. These coatings comply with the present EPA regulations.

Specifically, the feasibility research resulted in the following basic accomplishments:

-It was demonstrated that silicone-modified polyurethane copolymers could be synthesized and characterized.

-The final graft copolymers, when mixed with a modified aliphatic polyurethane, TEOS, titianium dioxide, and a catlayst produced stable dispersions.

-These formulations, after mixing with water, could be spray painted onto aluminum panels to produce hard, adherent films which cured in the required times.

Several of the coatings performed well in the wet adhesion, yellowing, and MEK rub tests.

This Phase I research program has established the feasibility and promise of the overall technology. An expanded Phase II program, if undertaken, should result in a practical and marketable protective, one-component, water-borne coating.

5.0 PROPOSED FUTURE RESEARCH

The positive results of this work provide a solid foundation for an expanded research program in Phase II. It is recommended that the next research phase include, at a minimum, the following parts.

1. A larger number of coating formulation samples and a more detailed examination of specific coating formulations. This will allow us to determine the best composition to achieve the greatest durability.

2. An examination of different additives (pigments, fillers, defoamers, coalescing agents, etc.) to see how they affect the coatings' usability.

3. Determine binder resin structure-property relationships.

4. Determine effect of pH and pH buffer systems on the binder resin kinetics.

5. Perform long-term tests of selected coatings on naval air and ground vehicles.

6. Establish the shelf-life and stability of the formulations.

7. Try other commercially available aliphatic polyurethanes in place of QThane QC4559.

The successful completion of this research program, through Phase II will result in a significant advance in the state of the art of one-component, water-borne coatings.

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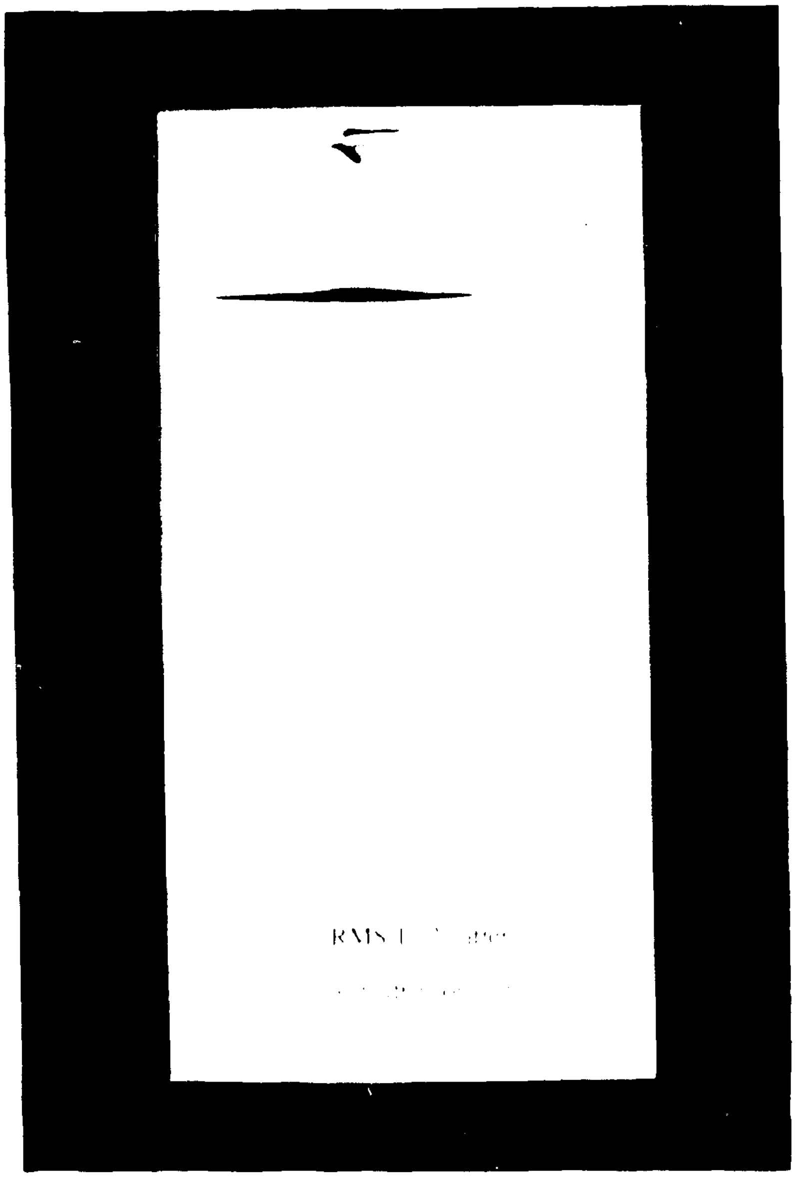
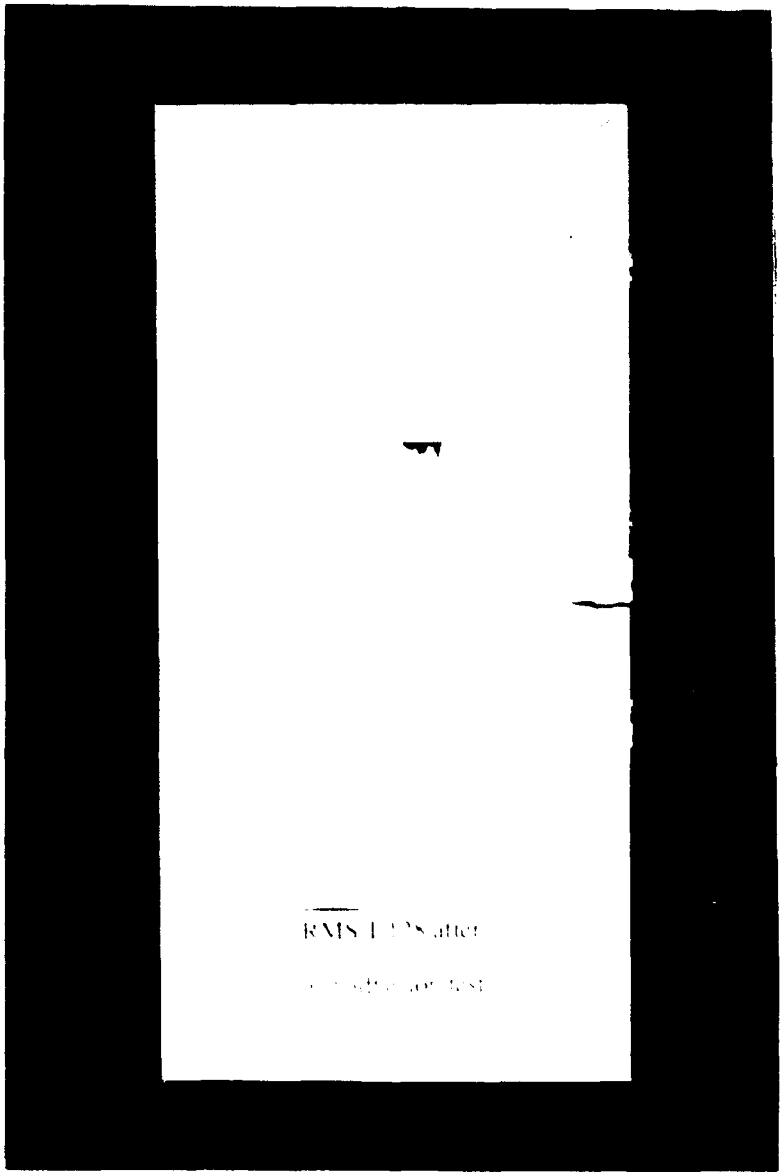
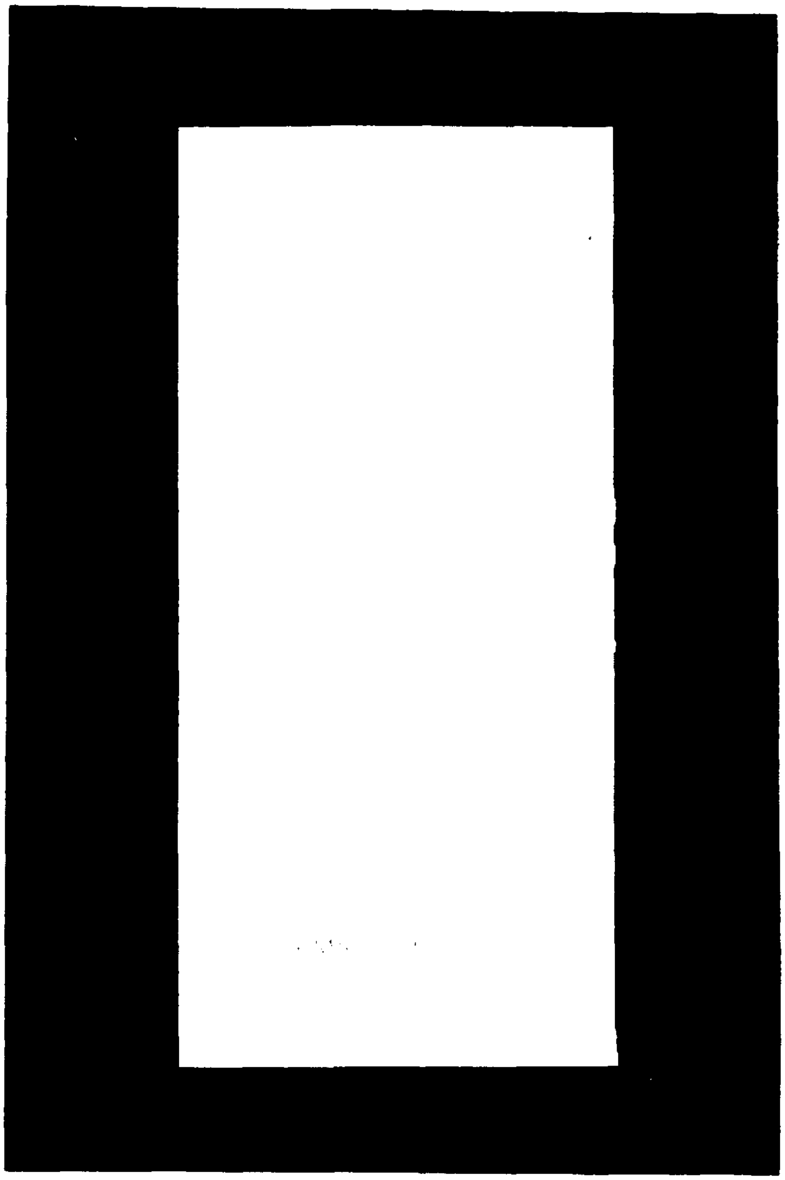
APPENDIX I: Pictures After Wet Adhesion Tests



RMS-I-127 after wet adhesion test



RMS-I-128 after wet adhesion test



RMS-I-129 after wet adhesion test

APPENDIX II: FTIR Data

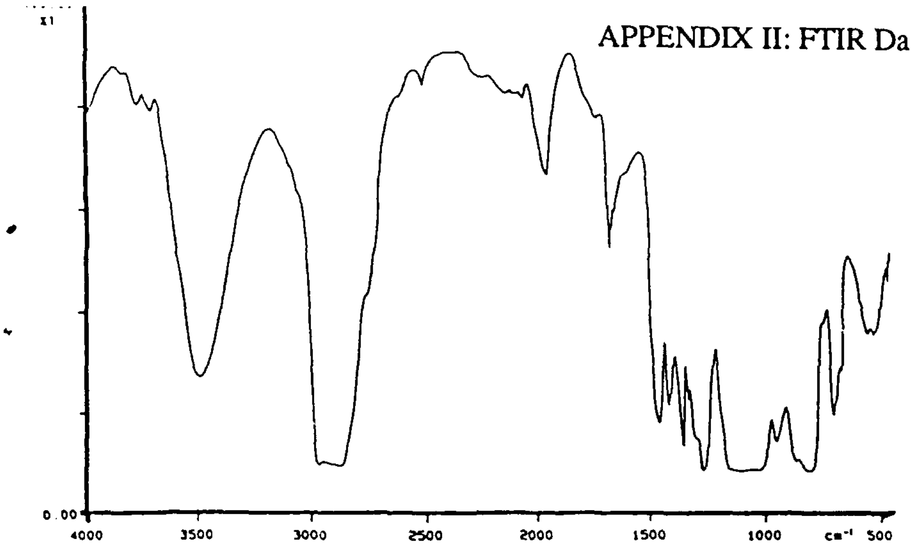


FIGURE Ia: PS-555 alone

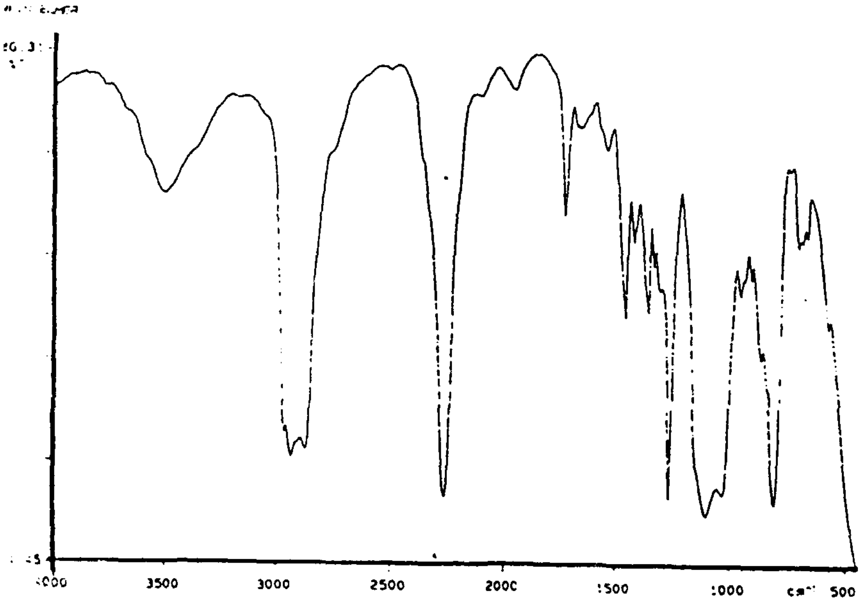


FIGURE Ib: PS-555 and diisocyanate

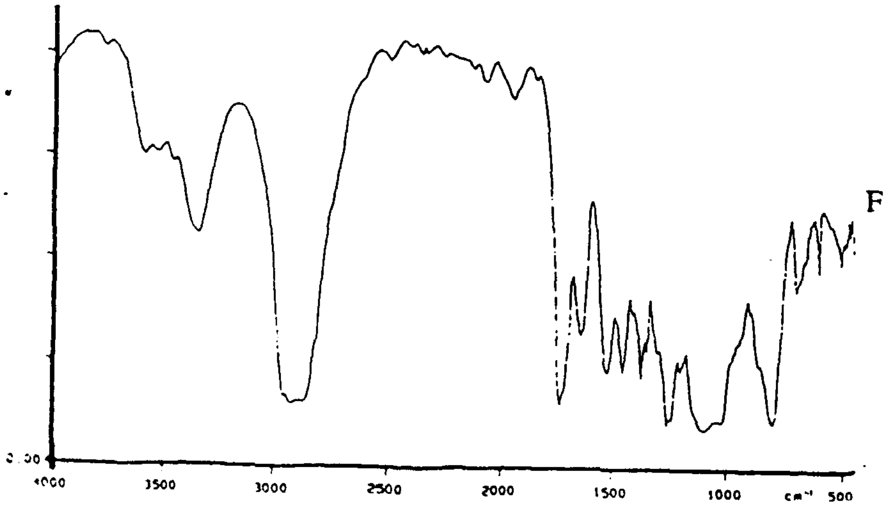


FIGURE Ic: PS-555, diisocyanate, silane, and PGMEA

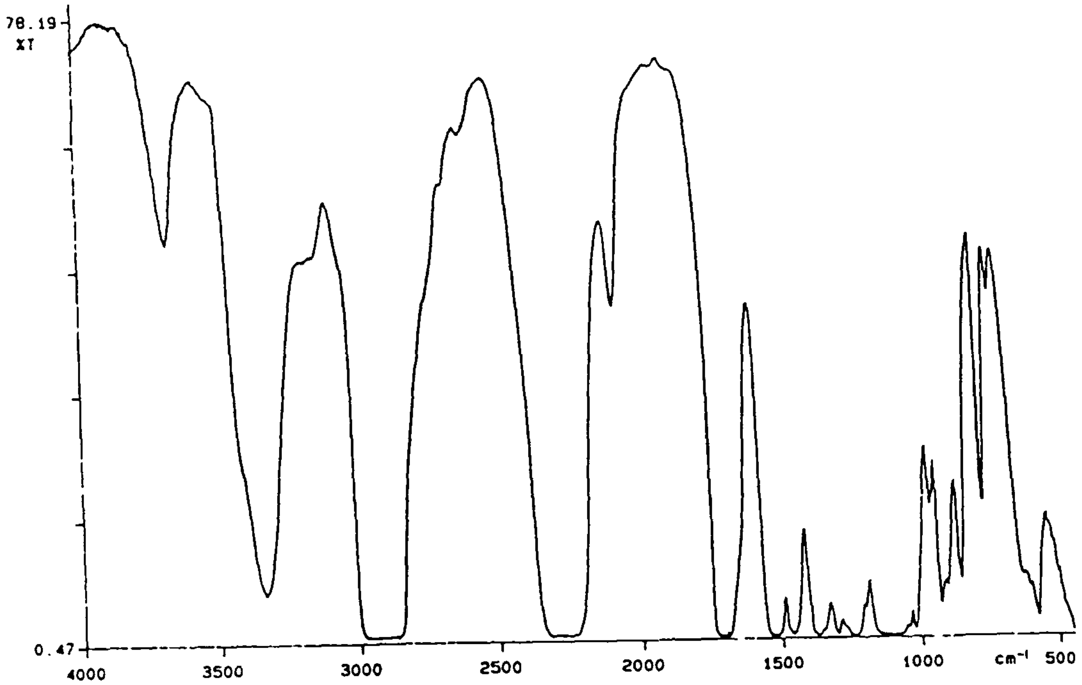


FIGURE IIa: Quinn QC 4559 alone

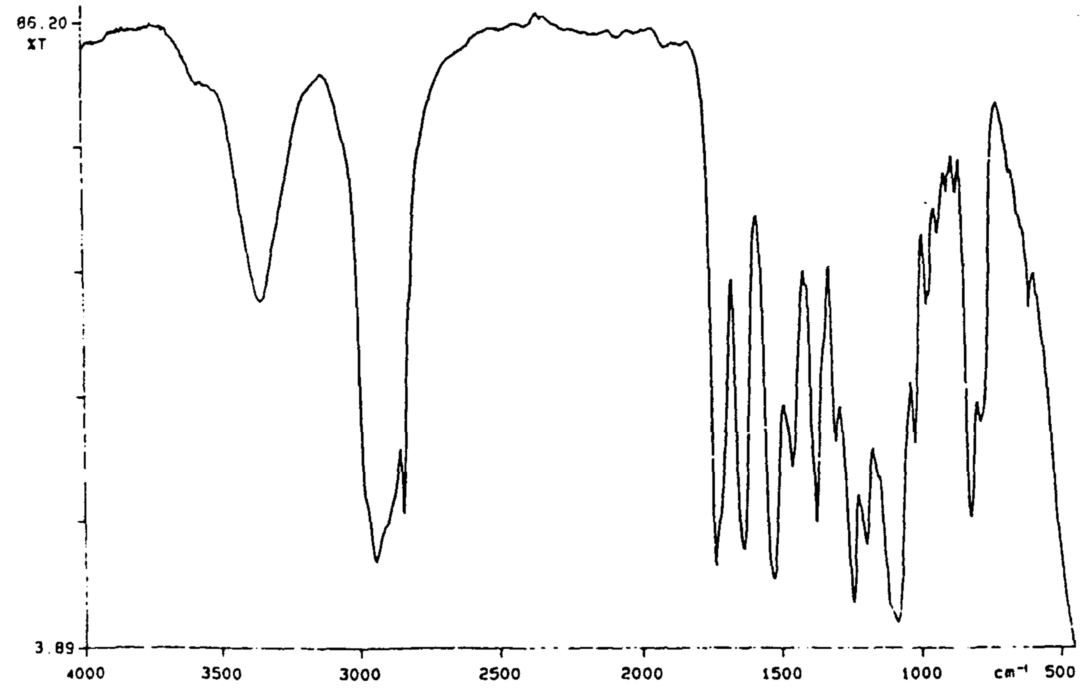


FIGURE IIb: Quinn QC 4559 after reaction with silane and PGMEA

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