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THE SYNTHESIS OF CONDUCTING POLYMERS FOR CORROSION PREVENTION

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ABSTRACT

The formation of an electrically conducting form of polyaniline by the oxidative polymerization of aniline was studied. Optimum yield and conductivities were obtained by treating aniline in 2 molar hydrochloric acid at 0 - 5°C with ammonium persulfate in a 1.15 mole ratio. The yield was 37.6% of theory and the conductivity of the product was 10.5 S cm^{-1}. This material was formulated into epoxy and acrylic coatings which were also electrically conductive.

TABLE OF CONTENTS

1. INTRODUCTION

1.1 BACKGROUND

The seacoast environment of the Kennedy Space Center is extremely corrosive to mild steel ground support equipment and structures. It had previously been established that the most satisfactory protection was afforded by an untopcoated, zinc-rich coating which utilizes an inorganic silicate binder. Unfortunately, this coating does not stand up to the high concentrations of hydrochloric acid in the effluent gasses from the shuttle booster engines. This has resulted in very high maintenance costs.

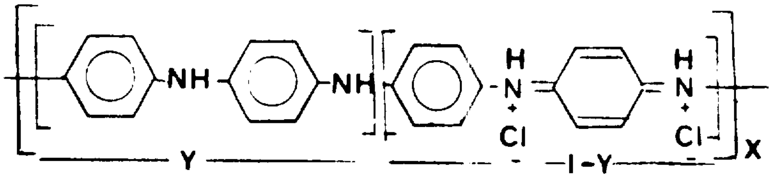
In the search for an acid resistant protective coating some consideration has been given to electrically conductive polymers. Although this is a very new field, there are several references which suggest a potential application of conductive polymers in corrosion control (1), (2), (3). Most of this work has involved a conductive form of polyaniline termed the "emeraldine salt." However, some of the most recent reports suggest that the 3-alkyl thiophenes might be superior to polyaniline in having a higher anodic potential (3) and improved processability of the polymer (4).

Despite the potentially improved properties of the polythiophenes, it was decided to start the KSC conducting polymer program with a study of polyaniline. The principle reason for this decision was the ready availability of starting materials, reagents and suitable lab equipment for the synthesis of polyaniline.

1.2 PRIOR WORK - POLYANILINE

The oxidation of aniline to polyaniline was first reported in 1840 (5). The product was known as "aniline black" and was used as a textile dye for many years. Between 1907 and 1910, Green and Whitehead (6) in England and Willstatter and Moore (7) in Germany studied the chemical structure of polyaniline. The structure has finally been elucidated and confirmed by an independent, unambiguous synthesis in 1987 by Wendl et al (8). The electrical conductivity of certain members of the polyaniline family were first reported by a French group in 1967 (9). More recently MacDiarmid (10) has reinvestigated the conductive form of polyaniline and found potential applications in lightweight, high energy density batteries and in corrosion control.

The electrical conductivity of polyaniline is a function of its oxidation and protonation states. the most conductive form is known as the emeraldine salt and exhibits conductivities in the metallic regime (5 - 10 S cm^{-1}). It has the structure



where y represents reduced or benzenoid units and 1-y represents oxidized or quinoneimine units. A polyaniline composed entirely of reduced units is colorless and an insulator; a polyaniline composed entirely of oxidized units is black in color, an insulator and readily hydrolyzed. The most conductive form, the emeraldine salt is blue-green and has equal numbers of the reduced and oxidized units (10). It appears that the conductivity is not related to the molecular weight (8), (11), indicating that the dominant charge transport mechanism is via intermolecular hopping.

Polyaniline is formed by the oxidative polymerization of aniline. It can be synthesized electrochemically on a platinum or steel anode, or by various chemical oxidizing agents. The electrochemical process yields a film on the metal. The chemical oxidation results in a powder which can be compressed into a pellet or incorporated, with a binder, to form a cohesive coating.

1.3 OBJECTIVES

The basic objective of this phase of the project was to synthesize a conductive polyaniline, formulate it in a coating and then prepare specimens for corrosion testing. The overall plan for the project is depicted in Figure 1.

2. EXPERIMENTAL

2.1 SYNTHESIS

The first task was the development of a practical laboratory process. Table 1 lists some of the procedures reported in the literature and in patents. Those procedures which gave conductive polyaniline were marked by extremely low yields(less than 1 gram of product per 500 ml of reactor space). The initial lab work therefore was directed towards developing a procedure which would give a reasonable amount of a conductive

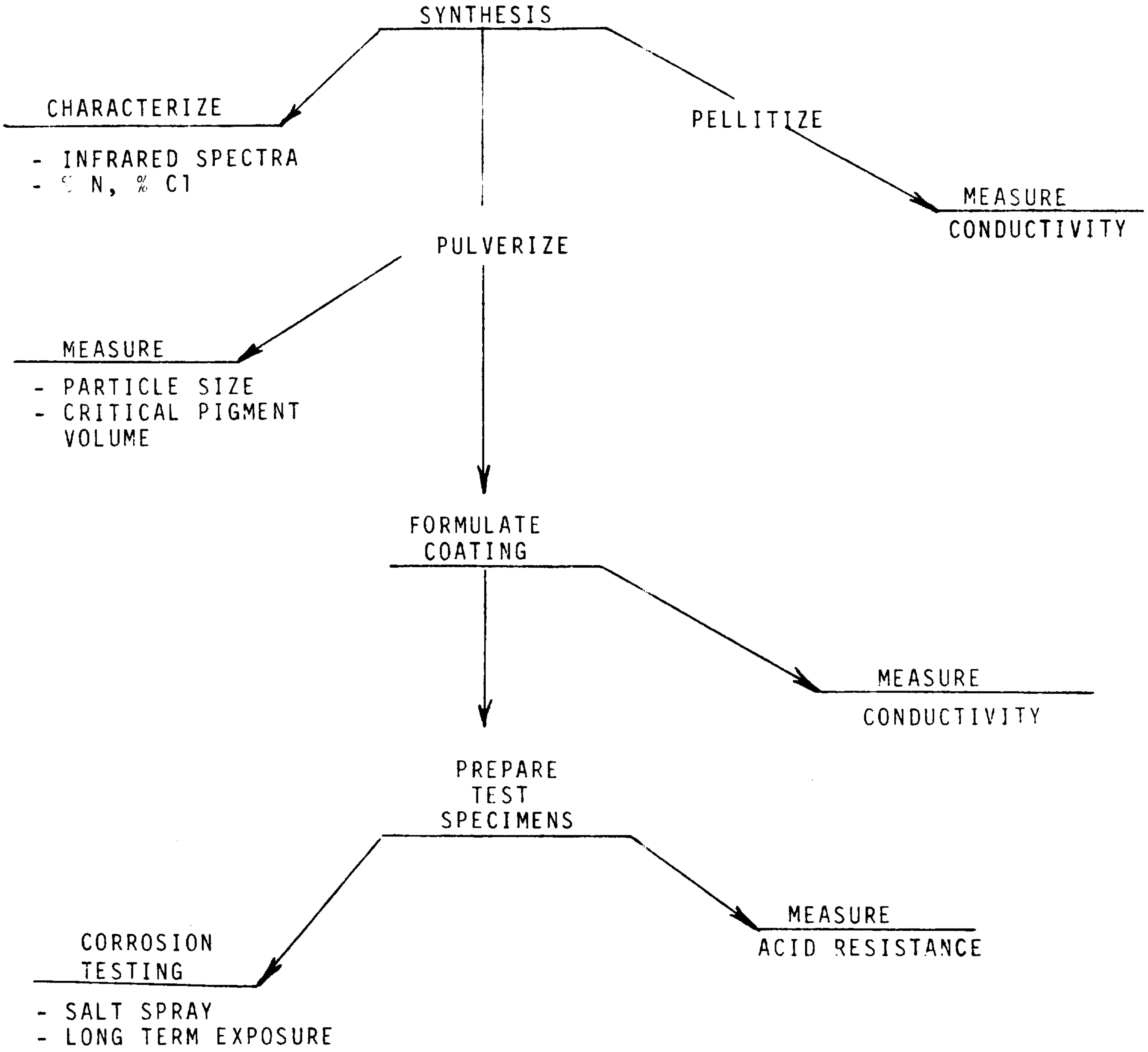


FIGURE 1 PROJECT PLAN

material. The oxidizing agents used included ammonium persulfate, hydrogen peroxide and potassium dichromate. These reactions were run at 0° to 5°C, in dilute hydrochloric acid. The insoluble product was filtered, washed, dried to a constant weight under vacuum, and pulverized in a ball mill.

2.2 PRODUCT CHARACTERIZATION

The infrared spectra of the partially oxidized forms of polyaniline are marked by absorption peaks at 1598 and 1500 cm^{-1} which are attributed to the imine and the amine groups respectively. This affords a qualitative indication of the oxidation state of the polyaniline. The atomic ratio of total organic nitrogen to ionic chloride can be used as a more quantitative measure of the oxidation and protonation states of the product. This is based upon the observation that in 2M hydrochloric acid only the imine nitrogens are protonated (10).

The powdered products were compressed into pellets and the conductivities measured by the four probe method.

2.3 FORMULATION OF COATINGS

To obtain a coating with maximum conductivity it is necessary to have the proper ratio of conducting pigment to binder This is called the "critical pigment volume concentration" and is defined as that level of pigmentation in a dry film where just sufficient binder is present to fill the voids between the pigment particles. This value is considered to be a property of the pigment and independent of the binder. It can be measured by ASTM 1483.

The binders to be used in this phase of the project include an epoxy cured with a polyamide, an acrylic latex, an epoxy cured with a thiol and a chlorinated rubber.

2.4 CONDUCTIVITY MEASUREMENTS

The conductivity of the various batches of polyaniline were made by a 4-probe Van der Pauw method on a compressed pellet of material. The pellets were formed by compressing in a 0.50 inch diameter press at 37,500 psig for 5 minutes at room temperature. The measurements were made on a Keithley Model 196 System DMM.

The conductivity of the cured formulated coatings will be made by the method described in MIL-P-26915A. This method consists of spraying the coating on two aluminum foil electrodes located 1/4-inch apart on a flat glass plate. When dried and cured, the resistance across the electrode gap is measured.

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2.5 CORROSION STUDIES

Sample panels will be prepared using the formulated coatings and evaluated by the salt spray (ASTM B117-85) and long term exposure.

3. RESULTS AND DISCUSSION

The results of the synthetic work are presented in Table 2. The product of Run 19, where potassium dichromate was used on the oxidant did not show the infrared absorption peaks that are characteristic of the emeraldine salt form of polyaniline. Run 17, where hydrogen peroxide was the oxidant gave the highest yield of product but the lowest conductivity. The results of the five runs using ammonium persulfate indicate that it is not necessary to use the very low ratios of oxidizing agent to aniline that have been reported in the literature. A comparison of Runs 23 and 25 suggest that a blanket of an inert gas allows more precise control of the oxidation state of the product.

Polyaniline from Run 7 was used to estimate the critical pigment volume concentration with shell epoxy resin Epon 1001 CX 75 as the vehicle. An average value of 0.62 grams of polyaniline to 1.0 gram of resin was obtained.

Using this value for the critical pigment volume concentration paint formulations were prepared using Shell chemical formulation SC: 97-76.608 and Mobile Paint Manufacturing Company acrylic latex, clear base 1412-40. These coatings were painted on glass slides. After curing both coating formulations were very conductive but were visibly non-uniform and marked by holes and voids. The actual, measured conductivity values are therefore not reported, since they represent flawed samples.

In order to prepare coatings which have an optimized, uniform and reproducible conductivity it will be necessary to grind the polyaniline to a specific particle size. The measurement of particle size microscopically was hampered by a clumping problem. Particle sizing by sieve methods should be possible when larger quantities of material are available.

4. CONCLUSION

A procedure is now available for the preparation of highly conductive polyaniline in sufficient quantities to formulate coatings and prepare specimens for corrosion testing.

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TABLE 1

PREPARATION OF CONDUCTIVE POLYANILINE LITERATURE REPORTS

OXIDIZING AGENT	MOLE RATIO OXIDANT/ANILINE THEORY	ACTUAL	YIELD, % OF THEORY	CONDUCTIVITY S cm^{-1}	REFERENCE
$(NH_4)_2 S_2O_8$	1.25	0.23	(3.6)*	5	12
$(NH_4)_2 S_2O_8$	1.25	1.15	(37.6)*	12.5	13
H_2O_2	1.25	1.29	(73.0)*	--	6
NaOCl	1.25	4.0	86	--	14
$K_2Cr_2O_7$	0.42	0.116	--	2	15

*YIELDS NOT REPORTED IN LITERATURE REFERENCE. LISTED YIELDS ARE THOSE OBTAINED IN THIS STUDY UPON REPEATING THE REFERENCED PROCEDURES.

TABLE 2
LAB PREPARATIONS OF POLYANILINE

RUN	OXIDIZING AGENT	MOLAR RATIO OXIDANT/ANILINE	YIELD, % OF THEORY[1]	CONDUCTANCE $S\ CM^{-1}$
7	$(NH_4)_2\ S_2O_8$	1.25	34.3	2.5
11	$(NH_4)_2\ S_2O_8$	0.23[2]	--	
15	$(NH_4)_2\ S_2O_8$	0.23	3.6	--
17	H_2O_2	1.29	72.8	0.6
19	$K_2C_2O_7$	0.11	69.7[3]	--
23	$(NH_4)_2\ S_2O_8$	1.15	27.5	6.2
25	$(NH_4)_2\ S_2O_8$	1.15[4]	37.6	10.5

1. BASED ON ANILINE CHARGED TO REACTION
2. THIS IS THE MOLAR RATIO USED BY MACDIARMID'S GROUP
3. INFRARED SPECTRA LACKS 1598,1500 CM^{-1} PEAKS.
4. REACTION IN NITROGEN ATMOSPHERE.

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