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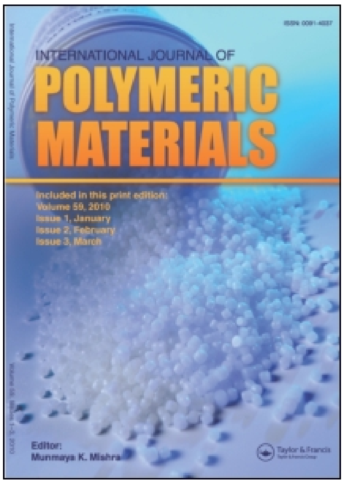

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Diamine-Quinone Polymers as Effective Anticorrosive Coatings†

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Quinone-diamine polymers have unusually strong affinity towards metals. The affinity is sufficiently strong to displace water from wet and rusty metal surfaces. The potential of these polymers as anticorrosive coatings is reviewed.

KEY WORDS Polymers, coatings, corrosion, quinone diamine

INTRODUCTION

Significance of corrosion as a major problem effecting the life expectancy of metallic structures, adversely, with its consequent economic impact cannot be overlooked. Hence, throughout history people have attempted to control corrosion using different coatings. Over the years, especially after the scientific basis of corrosive phenomena have begun to be understood, many quite satisfactory approaches, such as chromate and phosphate treatments, use of various zinc compounds as primers etc., were implemented. Newly emerging emphasis about environmental and health concerns, however, make some of these approaches impractical for the future. This leads to a continuous search for alternative materials and procedures that will be environmentally acceptable and have good anticorrosive characteristics.

RESULTS AND DISCUSSION

A family of polymers that are produced by reacting diamines with quinones have some unusual characteristics that satisfy many of the requirements expected of anticorrosive coatings.[1-4] Two of these characteristics that are by far the most significant for coating applications are: (1) their extraordinary affinity towards all metals, including gold and platinum, and their alloys, strong enough to displace water from wet, rusty steel surfaces; and (2) becoming water-repellent after curing.

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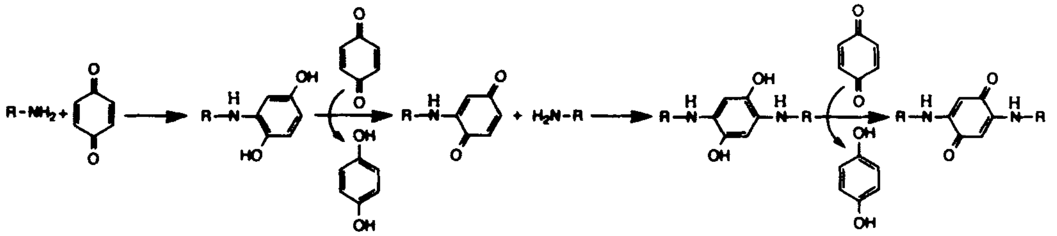
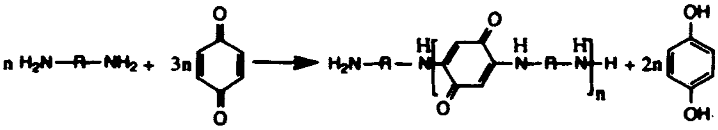
†This is communication #13 of the series: Quinone-amine polymers.

The reaction between an amine and quinone occurs spontaneously, according to the following scheme:



The first step leads to the formation of a monoamine substituted hydroquinone, which cannot react with a second amine, unless it is first oxidized to a monoamine substituted benzoquinone.

Because the introduction of an amino group lowers the redox potential of the ring, even the available free quinone can act as the oxidizing agent, simultaneously producing a free hydroquinone molecule. Reaction with the second amine yields a disubstituted hydroquinone which again is oxidized to a disubstituted benzoquinone. Thus it is clear that the reaction requires an oxidizing agent to proceed and for each final product containing one benzoquinone three benzoquinone molecules must be used, two of which are simply reduced to hydroquinone. If a diamine is used in this reaction one obtains a linear polymer:



This reaction, too, occurs very easily, starting with a reactant ratio of diamine:benzoquinone = 1:3, sometimes even at 0°C or below and is over within 3–5 hours. The progress of the reaction can be followed by UV spectroscopy (Figure 1). Use of excess benzoquinone for polymer synthesis is definitely not an attractive method because it results in the waste of two thirds of a precursor. Some of the produced hydroquinone remains bound to the polymer as seen in Figure (1c). Furthermore being volatile with a pungent odor and considered "caustic," benzoquinone is less desirable as a precursor than hydroquinone. Consequently several years ago the synthetic procedure was changed, in favor of hydroquinone as the starting material. This necessitated the selection of an external oxidizing agent, which after a long search led to the choice of calcium hypochlorite, due to its effectiveness and ease of removal after the reaction. With this change the reaction is carried out in two steps[5]: (1) oxidation of hydroquinone to benzoquinone and (2) reaction with the diamine.

Under these circumstances the reaction is run stoichiometrically and no hydroquinone remains unused and bound to the polymer (Figure 2).

Depending upon the nature of diamines and quinones, products with widely varying properties are obtained: polymers vary from soft, flexible, tough to insoluble and even infusible. All polymers are insoluble in water before curing. Solubility

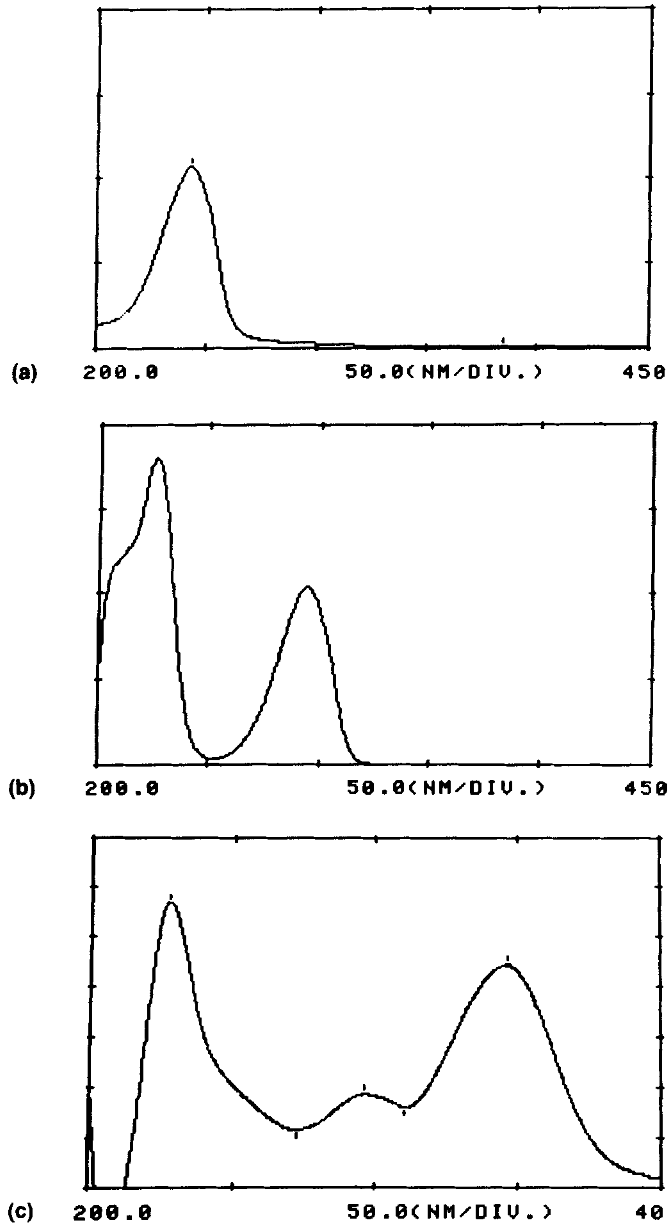


FIGURE 1 UV profiles of 1,4-benzoquinone (1a), hydroquinone (1b) and the formed polymer (1c). It is clear that some hydroquinone is found in the polymer synthesized with benzoquinone:diamine = 3:1.

in organic solvents also varies greatly[6] (Table I). Insolubility of ethylenediamine and 1,12-diaminododecane based polymers can be attributed to their excessive crystallinity.

Preparation of copolymers, using two different amines (Table II) or use of other quinones, such as 2-phenylbenzoquinone, can be used to increase the solubility of

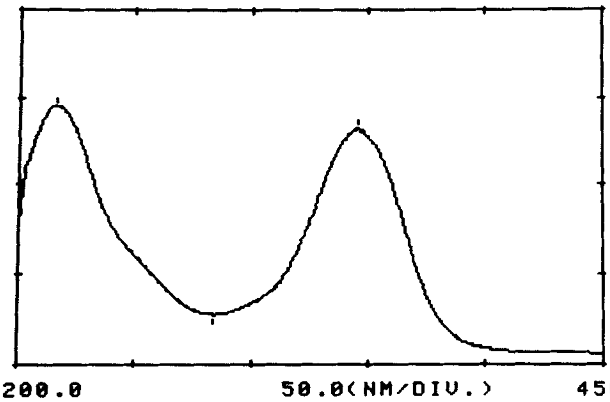


FIGURE 2 UV profile of the polymer prepared with hydroquinone = diamine = 1:1, using calcium hypochlorite as the oxidizing agent. No hydroquinone is present in the polymer.

the polymers (Table III). All soluble polymers exhibit extraordinary affinity towards metals. This is due to "chemisorption," involving the quinone oxygens and imino nitrogens. Studies by Hubbard and co-workers,[7] using cyclic voltammetry, have demonstrated that a volatile compound, quinone, binds to gold or platinum, with such affinity that it resists 10^{-9} Torr vacuum. These polymers can also displace machine oils from metals.

The polymers can be cured either thermally, with or without the addition of diamines, or chemically, at ambient temperature or at higher temperatures, up to 150°C for 3–5 hours. Thermal cure occurs by the introduction of amino or imino nitrogens at the vacant sites on the quinone ring.

Since each repeat unit contains two imino nitrogens, the polymers can also be cured using any multifunctional chemical that is capable of reacting with active hydrogens: difunctional epoxides, epoxy resins, titanates, aziridines etc. Isocyanates cannot be used because even the most sluggish ones react so rapidly that immediate cure takes place while mixing. Their ability to react with epoxy-novolac resins, stoichiometrically, has been exploited for ambient cure, which takes about a week to complete. This composition eliminates the brittleness of epoxy resins and a panel coated with a 1 mil thick coating can be bent on an 1/8" mandrel. The polymers can also bind to siliceous materials, such as glass, concrete etc. Anticorrosive characteristics have been tested on two different polymers: (1) Jeffamine® D-400-benzoquinone polymer, and (2) 1,12-diaminododecane-2-phenylbenzoquinone polymer.

The first polymer is soluble in many solvents, however, since a mixture of xylene:n-butanol = 4:1 dissolved the polymer and was found to have the requisite dry-time, viscosity and flash point specified by the U.S. Navy, which supported this investigation, all studies were performed with the polymer dissolved in this mixture, which can be prepared with 85% solid content. When mixed with stoichiometric amount of epoxy-novolac DEN 438 or EPON 828, the mixture has a pot life of 6–9 hours, dry-time of 6–8 hours and although curing is nearly complete after 24 hours, best results are obtained after 7 days, at room temperature.

Heating at 110–150°C for 3–5 hours affords equally good quality coatings more

TABLE I

Solubility profiles of quinone-diamine polymers

Diamines Used Solvents	Ethylene diamine	1,12-diamino-dodecane	m-Phenylene diamine	2,4-diamino-5 tert-butyltoluene	1,4-diamino Cyclohexane	Trimethyl-hexa-methylenediamine	Jeffamine(R) D-2000	Jeffamine(R) D-400	APB(a)	Lysine
Acetone	0.04	0.28	1.80	Sol	Swell	1.11	Sol	Sol	0	0
n-Butanol	0.01	n.d.(b)	n.d.	0	0	1.09	Sol	Sol	0	0
Chloroform	0	0.12	n.d.	Sol	Swell	5.83	0	0	0	0
DMA	1.40	0.11	6.56	Sol	0.90	9.34	Sol	Sol	Sol	0
DMF	1.15	0.21	4.32	Sol	1.03	4.56	Sol	Sol	0	0
Dioxane	0.02	0.11	2.96	Sol	1.23	2.85	Sol	Sol	0	0
DMSO	3.15	0.30	7.25	Sol	Swell	16.26	Sol	Sol	Sol	0
Ethanol	0.05	0.1	0.56	Sol	0.23	n.d.	Sol	Sol	0	0
MEK	0.09	0.32	2.48	Sol	0.77	3.74	Sol	Sol	0	0
NMP	1.13	0.38	8.36	Sol	Swell	8.9	Sol	Sol	0	0
THF	0.09	0.29	3.29	Sol	0.47	3.11	Sol	Sol	0	0
Xylene	0.04	n.d.	n.d.	Sol	0.14	n.d.	0	0	0	0
Concd sulfuric acid	n.d.	Swell	0.65	n.d.	5.85	6.91	n.d.	n.d.	n.d.	0

(a) Ref #2

(b) not determined

TABLE II

Increasing solubility of polymers by copolymers formation, % w/w

Copolymers, two amines:	DMSO	NMP	MEK	Ethanol
Jeffamine® D-2000 - ethylenediamine (1:1)	nd	nd	23.0	18.0
Jeffamine® D-400 - 1,12-diaminododecane (1:1)	nd	nd	9.2	3.65

n d: not determined

TABLE III

Dependence of polymer solubility on quinone structure, % w/w

	ACETONE	n-BUTANOL	XYLENE	THF	MEK	CHLOROFORM	DMSO	DMF
1,12-DIAMINODODECANE: p-BENZOQUINONE	0.28	----	----	0.29	0.32	0.12	0.3	0.21
1,12-DIAMINODODECANE: 2-PHENYLBENZOQUINONE	11.3	8.3	10.0	Sol.	11.7	Sol.	Sol.	Sol.

TABLE IV

Results of salt-fog tests

The results of salt fog test run at DTRC[(a)] on paint samples. They were run for 500 hours and evaluated against Navy Formula F-150 and Devran 235 as controls.

Rusty Steel Substratum	Sample	Propeller Bronze Substratum
100% intact	1	99% intact
100% intact	2	100% intact
Disappeared entirely	3	100% intact
90% intact	4	98% intact
100% intact	5	95% intact
100% intact	F-150	----------
100% intact	Devran 235	----------

(a) David Taylor Research Center

Key to samples #1: Jeffamine®-p-benzoquinone/DEN 438; #2: Jeffamine®-p-benzoquinone/TYZOR® TBT; #4:Diaminododecane-phenylbenzoquinone; #5: Diaminooctane-phenylbenzoquinone.

TABLE V

Electrochemical impedance spectroscopy

In the frequency range (60kHz - 0.1 Hz), the two coating systems exhibited purely capacitive responses, with no significant variation of response during 2,000 hour immersion period.

This result indicates that these polymeric materials did not take up any significant quantity of electrolyte during testing.

THUS THESE COATING SYSTEMS ARE CLEARLY EXCELLENT BARRIERS TO THE UPTAKE OF WATER/ELECTROLYTE.

TABLE VI

Combined corrosion/weathering test

Weathering Segment	Corrosion Segment
168 hours UV light/H_2 condensation as follows: 4 hours UV light [UVA-340 bulbs] at 60°C alternating with, 4 hour H_2O condensation at 50°C.	168 hours wet/dry cycle corrosion testing as follows: 1 hour spray [0.35wt% $(NH_4)_2SO_4$ + 0.05wt% NaCl electrolyte, at ambient temperature.

TOTAL TEST DURATION: 4 WEATHERING + 4 CORROSION CYCLES (1344 hours).

THESE SYSTEMS EXHIBIT GOOD CORROSION PROTECTION REMOTE FROM SCRIBE LINE DAMAGE.

quickly. The mixture can be applied using all standard methods, such as spraying, brushing etc. It coats "tight-rust" and the films produced are free of pin-holes. If cast on Teflon covered surfaces one can obtain free standing films. 1 mil thick coating resists abrasion, according to ASTM D968-81.

Its impact resistance, too, is quite impressive: polymer remained attached to a rusty steel panel coated with this polymer, after it has been in the salt-fog chamber for 500 hours, followed by an 180 inch-pound impact, even though the metal broke during the impact. Corrosion resistance was tested both by the David Taylor Research Center and Sherwin-Williams Company Corrosion Science Laboratory. In both cases the thickness of the coatings were 1–2 mils.

As seen in Table IV both polymers have survived 500 hour exposure to salt-fog, both on rusty steel and propeller bronze. The one partial failure was due to a new polymer based on 3,5-diaminobenzoic acid. F-150 and DEVRAN 235 are U.S. navy standard epoxy coatings used as controls. They, however, cannot be applied to wet surfaces. Two different tests were performed at the Sherwin-Williams Company: (1) AC impedance test, and the (2) Sherwin-Williams combined corrosion/weathering test. The conditions of the tests and the conclusions are presented in Tables V and VI.

Several years ago coated panels were exposed to short wave UV for 400 hours, at 2″ distance, without developing any blisters or cracking. Coated panels were also exposed to the atmosphere, on the roof of the laboratory, located in North Philadelphia, up to 18 months, without any blister formation.

The films also have very good chemical and solvent resistance: no organic solvent, including SKYDROL®, as well as 1N sodium hydroxide have any deleterious effect on the films, after several weeks of immersion.

The only difference between the Jeffamine and 1,12-diaminododecane based polymers is the latter's being a single component system, not requiring any curing agent, although a curing agent can also be used, if desired. The polymeric films can be coated by any solvent-based paints, however, water based latexes cannot be used because the polymer surface cannot be wetted by water.

On the other hand, these polymers can bind to all conventional paints. When used as a primer these polymers were found to increase the adhesion of epoxy-coatings twofold and vinyl-coating threefold, according to studies performed at the David Taylor Research Center. These polymers are also non-flammable. According to studies of Jenkins *et al.*,[8] some of these polymers also conduct heat. Similar tests were also conducted on aluminium panels at the Naval Air Development center, at Warminster, PA, several years ago and the results were found to be satisfactory.

CONCLUSIONS

Quinone-diamine polymers that have unusually strong affinity towards metals and alloys strong enough to displace water from wet, rusty metal surfaces, due to chemisorption, have been shown to provide excellent anti-corrosive protection to metals. They are very easy to produce and can be cured either chemically, at ambient temperature, thermally or by a combination of both, becoming water-repellent. Most are flexible, all have very good solvent, impact and abrasion resistance. They also resist exposure to short wave UV and they can be cast into free standing films.

These properties make them good candidates for being used as water-displacing primers and coatings, water-resistant adhesion promoters, to protect reinforcement bars used in highway and bridge construction from corrosion, to impregnate wood to impart dimensional stability, packaging of electronic components, metallization of plastics and metal-polymer composite, high temperature performing coating and adhesive development.

Some of these possibilities have already begun to be exploited: U.S. Navy has started to use some polymers in their ships for long-range field tests. A generic process for metallization of plastics that require no specialized equipment was developed, using these polymers.[9] Other applications require the optimization of conditions for each special use. Development of high temperature performance coatings and adhesives require funding to carry out the studies.

Full commercialization will have to wait until the scale-up process is achieved with the help of a producer.

Acknowledgment

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