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New Anti-Corrosive Coatings with Resin-Bonded Polyaniline and Related Electroactive Groups

Final Report

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EXECUTIVE SUMMARY

It is already known that polyaniline (an electroactive polymer) functions as a corrosion inhibitor for steel and in view of the fact that it is known to perform in the presence of hydrochloric acid, it has been considered likely that it may be useful to NASA for protecting launch structures at KSC which are exposed to not only continual ocean-side salt spray but also to hydrochloric acid at the times that solid-fuel boosters are fired. The currently used zinc-rich silicate-bonded coating is not wholly protective against the hydrochloric acid. Water pollution from zinc salts is another concern. Other earlier and concurrent NASA sponsored projects have been focussed on polyaniline specifically. Our project, administered for NASA by Dr. K. Thompson of KSC and these more-specifically polyaniline-related projects are included in a CRADA coordinated by Dr. F. Via of Akzo Nobel. A parallel project at Polytechnic under Prof. K. Levon concentrated more specifically on polyaniline with various dopants.

Our exploratory project reported herein was aimed at broadening the range of such corrosion inhibitors, to give protective paint compounders a wider latitude for adding corrosion inhibitors having polyaniline-like performance, and thus we diverged in several probing directions from polyaniline. Our working hypothesis was that physical variants of polyaniline, such as supported formulations on pigments or carriers, and chemical variants of polyaniline, including those having no electroconductive character, may have enhanced anticorrosion activity. We also hypothesized that small (non-polymeric) molecules having structures related to those occurring in polyaniline, may be active as corrosion inhibitors. We did preliminary testing, using an ASTM salt spray method at a nearby commercial paint testing laboratory.

Our most interesting findings were that a non-electroconductive meta-isomer of polyaniline showed some corrosion activity, suggesting that the features of the polyaniline molecule associated with conductivity are not necessary for the anticorrosion action. Also, significantly, small molecular weight aromatic diamines and diimines resembling the reduced and the oxidized repeating unit in polyaniline showed an interesting degree of anticorrosive activity, suggesting that the polymeric feature of polyaniline is not necessary for anticorrosion action. Since a variety of aromatic diamines, and in particular, N-substituted p-phenylenediamines are available on a commercial scale, and are known to undergo air oxidation to the diimines, this finding opens up a wide range of plausible anticorrosive additives, hitherto unrecognized, for formulation, by addition or coreaction, into metal-protective coatings. Their postulated mode of action would be to mediate or catalyze the oxidative passivation of steel, and perhaps also to aid the bonding of protective coatings to steel.

Our findings regarding the anticorrosive activity of N-substituted p-phenylenediamines also suggest a much broader hypothesis which proposed that redox systems with the correct redox potential and adequate reversibility and with good metal bonding or with the ability to be reacted into coatings, may provide anticorrosive activity by oxidative passivation of metals.

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Reports and Tables of Salt Spray Corrosion Tests Run at D/L Laboratories

Appendix: Technical Report from June 1995 to Nov. 1995; contains work done by Prof. Indra Varma on m-polyaniline, supported polyaniline on carriers and attempted addition reactions of polyaniline

Objectives

Our project was part of a CRADA (Cooperative Research and Development Association) involving Akzo Nobel as the industrial partner, KSC, Los Alamos, NRL as the government laboratories, and ourselves, Drexel and Ohio State. The objective, from KSC's point of view, was to find better ways to protect the steel structures from salt spray and the hydrochloric acid released from launching solid fuel boosters.

Our part of the overall CRADA was directed toward exploratory variants on the polyaniline theme, aimed in the general direction of increasing the practicality of usage in corrosion inhibitory coatings. We considered that enough work had been and currently was devoted to polyaniline as a coating polymer, so we addressed several divergent approaches which we considered to not be sufficiently dealt with elsewhere: (1) polyaniline on an inert carrier or on a commercial corrosion inhibitory carrier, in a pigment like mode, (2) substituted polyaniline having solubilizing substituents, and (3) diverse types of corrosion inhibitors "inspired" by the structure of polyaniline, but diverging from polyaniline. As the project proceeded, approach (1) became quickly deemphasized when we got our best results on a carrier which we found was already being studied at Los Alamos, approach (2) was deemphasized when our proposed chemistry did not work, with our attention turning to non-polyaniline molecules having some mechanistic or chemical relationship to polyaniline. This last approach (3), which we had contemplated even before the onset of the project (various discussions with Dr. F. Via at Akzo Nobel) became our main approach and proved to be fruitful in opening up a practical direction for anticorrosion coating R&D. We now believe that small molecules can have polyaniline-like character and may be more versatile for building into various types of corrosion resistant organic coatings.

Research targets: diverse corrosion inhibitors bearing some relationship to polyaniline

Polyaniline has been the subject of a large literature, including reviews on its anticorrosion properties (Wessling 1996; McAndrew 1997 are recent ones). On the other hand, to put it in context, a recent review on anticorrosion pigments by a leading expert (Hare 1996) does not even mention polyaniline, so other than the Ormecon product, it seems to have made no entry as yet into the marketplace as an anticorrosive.

Much attention had been originally been directed to the assumed relationship between the electroconductivity of doped polyaniline and its anticorrosion activity, but there are indications which point away from the electroconductivity viewpoint and merely require redox activity (McAndrew 1997, Kinlen et al., 1996).

Our viewpoint is that it is suggestive of a number of R&D directons in the anticorrosion field. Polyaniline has a number of features which place it at the intersection of several known groups of corrosion inhibitors. Many nitrogen compounds, especially strongly absorbed ones are known and used in preventing attack on steel during acid pickling (Schmitt 1994, Trabanelli 1994). Polymeric aniline derivatives with non-conjugated aliphatic linkages are known as corrosion inhibitors (Bacskai et al. 1988, Badran et al. 1985, El Sawy et al. 1994, Sumitomo 1984, to name a few). In contemplating the mechanism of action of polyaniline as a corrosion

inhibitor, we should bear in mind that several of these features may be contributing to its total action and even if one mode of action is demonstrable under one set of test conditions, that does not necessarily eliminate the other possible modes of action.

The broad class of amines encompasses many corrosion inhibitors. Regarding mode of action, information on solution inhibitors perhaps bears some relevance to materials which may be active in coatings. Such solution inhibitors include pickling inhibitors (for removal of rust or scale by use of acid with limited attack on the metal), additives used in salt for inhibition of corrosion on steel, and additives used in crude oil and petroleum products to prevent attack of acids on steel pipe. Some useful reviews of corrosion inhibitors are available (NACE 1993, Trabanelli 1987). Even simple aliphatic amines, both short and long chain, are active in various corrosion inhibitory modes in aqueous or oil solution (Rawat *et al.* 1987, Incorvia 1985) and dicyclohexylamine has had much usage as a vapor phase corrosion inhibitor for steel. Polyethylenepolyamines are said to be advantageous solution corrosion inhibitors for iron in hydrogen sulfide-rich petroleum waste waters in Russian studies (Podobaev *et al.* 1987). Simple arylamines including aniline itself are not devoid of activity. Electron density seems positively correlated to inhibitory activity (see papers in NACE 1993). Heterocyclic amines have had much attention as corrosion inhibitors and there are numerous patents on imidazolines, triazoles, etc. (see the general reviews for many examples). Particularly interesting is a study in which alkylacridine (3 rings) is more active than alkylquinoline (2 rings) which in turn is more active than alkylpyridine (1 ring) as a pickling inhibitor; this suggests that polyaniline viewed merely as a multiple ring arylamine should be expected to be active. Large flat molecules with multiple ring nitrogens seem to be very active; phthalocyanines, for example (Hettiarachi *et al.* 1989). Other than polypyrrole discussed above, there are only scattered reports of polymeric heterocycles as corrosion inhibitors. This would seem like a fruitful area for further work.

Polymeric anilines with no conductive or special electroactive features have been reported to have corrosion inhibitory action (as pickling inhibitors in hydrochloric acid); for example, a condensation polymer of p-toluidine and formaldehyde appeared particularly active (Kuznetsov and Valuev 1987).

The electroactive feature of polyaniline (i.e. existance of oxidized states having quinone imine rings either as such or as resonance states) is suggestive of the very active quinone-diamine condensation polymers (Reddy and Erhan 1994, 2 refs., Erhan 1996). These have, in many cases, aliphatic chains joining the quinone rings so cannot be electroconductive, but are nonetheless, potent corrosion inhibitory coatings. Erhan attributes this activity to very strong bonding of the quinone oxygen atoms to the metal, and notes that these polymers will displace water from wet rusted metal (a useful but not a unique property, shared with some commercially available corrosion inhibitory marine paints).

One conspicuous feature of polyaniline in its emeraldine base or doped form is its apparent ability to passivate iron by forming an oxide (Wessling 1994, Lu *et al.* 1995); Wessling plausibly theorizes that the reduced polyaniline is then reoxidized by air and thus acts as a catalyst for oxidative passivation of iron. If this is the mechanism of action, or one of the mechanisms of action, then polyaniline may be said to share the oxidative feature with other good corrosion

inhibitors such as the chromates, molybdates, or calcium nitrite amongst the inorganics, or zinc nitrophthalate amongst the organics (Hare 1996).

This highly generalized (some might say, overgeneralized) point of view suggests that there should be many reversible oxidants for iron or other corrosible metals which could serve as passivating inhibitors. A favorable molecular feature would be a capability for strong bonding to the metal by having high electron density at numerous points in the molecule. Flat or at least surface-conformable molecular structure should also be advantageous. The ideal might be a "molecular tile" having reversible redox chemistry, the oxidized form being able to oxidize iron, the reduced form able to be reoxidized by air. Electroconductivity may or may not be an advantage. Some critical range of redox potential is probably important; sources of such data are available in the polarography literature, and indeed redox potential is now reasonably predictable by molecular orbital calculations.

Initial approach and formulation of strategy

The project was initiated by discussions with informed persons at KSC and Akzo-Nobel, and literature reviews to supplement information collected prior to the project. We collected literature not only on polyaniline but on also related electroactive and non-electroactive relatives thereof, especially possible corrosion-inhibitory structures believed useful for attachment to epoxies. We were told by Ciba and Air Products technical service persons familiar with epoxy coatings that aromatic amine curing agents were known to be conducive to corrosion inhibition, but we have not located the documentation of this belief. We were told that the arylamine curing agents have been largely discontinued for industrial hygiene reasons, plus their generally slower curing action.

Noteworthy items found in our search included the following:

- Commercially available electroactive zinc nitrophthalate anticorrosion pigments from BASF
- Various aminoquinone polymers having anticorrosion properties published by Prof. S. Erhan at Albert Einstein Medical College, Philadelphia (Erhan 1996).
- A Russian report of *non*-conjugated polyaromatic amines reported active against HCl corrosivity. Various reports of non-polymeric amines as corrosion inhibitors against salt and HCl were found; the evaluations against HCl were mostly in connection with "pickling" where iron oxide is removed from steel (Kuznetzov and Valuev 1987, Schmitt 1994).

We initially decided to probe in several directions, to see what showed promise. These were: derivatizing polyaniline to make it more amenable to incorporation into coatings, by either putting functional groups onto it, formulating it with carriers or on corrosion-inhibitory commercial pigments, and then deviating from polyaniline to look at some related polymeric and non-polymeric arylamines.

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Attempted Derivatization of Polyaniline by Aliphatic Polyamines

For comparison and also for derivitization, polyaniline was synthesized in 58% yield by the known persulfate oxidation of aniline. We that the yield depended on duration as well as oxidant ratio (thus higher yields should be attainable). Details are in the Appendix.

We had predicted that polyamines would react with the quinonediimine part of polyaniline by the known Michael addition reaction. The object was to put good aliphatic amine groups onto the polymer to make it more likely that it would cure into epoxy coatings. However, reaction attempts at several temperatures with ethylenediamine or other aliphatic polyamines were unsuccessful. The polyaniline was recovered unchanged. Details are in the Appendix.

Polyaniline on a commercial corrosion inhibitory pigment and other carriers

Clean steel panels were coated with a formulation of polyaniline deposited from N-methylpyrrolidone onto commercial zinc phosphate corrosion inhibitory pigment and compared to the same loading of zinc phosphate without the polyaniline, each dispersed in a typical epoxy resin and, after curing with polyamine, immersed in hydrochloric acid. Simple jar tests were run in dilute hydrochloric acid but we could see no differences by optical microscopic examination of the exposed metal surfaces after a week.

Polyaniline coatings were similarly applied to another commercial corrosion inhibitory pigment (zinc phosphate-molybdate) as well as to an inert mineral filler(talc), with the objective of making more effective corrosion inhibitory pigments, using preformed polyaniline. Alternatively, polyaniline was made in situ and absorbed onto talc, silica and mica. These products were submitted to Akzo Nobel for testing, but a test methodology had not yet been developed there. Consequently, we submitted the formulations to the D/L Laboratories, NYC, a commercial paint testing laboratory with experience in compounding paint formulations and running the Salt Fog test. Methodology was in accordance with ASTM D 117. Other evaluation methods used are listed and explained in Report I/Table I. Results are reported in Table I. With our experimental formulations, the only favorable one was 7.7% PANi on fused silica, Siltex 44, which gave in 100 hours a rating of 10 (best) and 0% area corroded. At 200 hours, the rating was only 4 (22-26% area corroded) which was inferior to a commercial corrosion inhibitory pigment, BASF's SICOR SPO (zinc nitrophthalate/zinc phosphate).

Thus, our best results were on silica, a substantially inert carrier. We learned then that Los Alamos had come to the same system, and there was some published work (Stejskal *et al.* 1996) also with polyaniline and silica, so we discontinued this line of work in our program.

Meta-analog of polyaniline and other non-polyaniline aromatic polyamine polymers

To test our hypothesis that the quinonediimine feature of polyaniline is unnecessary for the corrosion inhibitory effect, we carried out a synthesis of the meta analog of polyaniline by a literature method. Details of this synthesis and characterization of the product are given in the Appendix (Technical Report for the period July 1- Nov. 30, 1995).

We also reviewed product directories to seek some commercially available polyaromatic amine to test our hypothesis that a conjugated polyarylamine structure is not needed for good corrosion inhibition of steel. We were thus able to obtain poly(4-vinylpyridine) as a commercial product from Reilly Chemical Co. (Indianapolis). We applied this polymer on to blast-cleaned steel and submitted it to Akzo Nobel (Dobbs Ferry, NY) for electrochemical corrosion testing.

Also to test our hypothesis that a conjugated polyarylamine structure is not needed, an oligomer of p-toluidine and formaldehyde, which should have -CH_2- linking groups between the rings, was made. This product, suggested to be a polymer by a Russian article which has no experimental details, appeared not to be a polymer but a crystalline dimer, o,o'-methylenebis(p-toluidine).

Comparative testing of commercial nitrophthalate pigment, m-analog of polyaniline, toluidine-formaldehyde product, polyvinylpyridine and quinone derivatives vs. polyaniline

A series of samples was formulated, as 7.8% formulations with 92.2% silica, at a pigment to binder solution ratio of 1:2 (pigment to solids ratio of 1:1) in a melamine-crosslinked polyester coating and run for an abbreviated (200 hours) salt fog test at D/L Laboratories. The data is in Report 2/Table 2. The corrosion test results were in the following sequence, from best to worst: zinc nitrophthalate (a BASF corrosion-inhibitory pigment); bisanilinobenzoquinone; the dibenzoate of benzoquinonedioxime; a p-toluidine/formaldehyde condensation product; the blank; the meta analog of polyaniline; polyvinylpyridine. PANi (emeraldine base) was almost inactive, and considerably worse than the blank. A commercial corrosion inhibitor, Irgacor 252, a Ciba benzodiazolyl compound, was totally inactive, worse than the blank.

These results show that the emeraldine base form of polyaniline may not be readily made effective when used as a pigment (as Wessling emphasizes, it may be very formulation-dependent). A number of smaller molecules such as the dianilinobenzoquinone or the benzoquinonedioxime diesters may be better in a pigment mode. The meta-analog of polyaniline, while not very impressive, did show more activity than polyaniline, so we may have made the point that the structural feature (p-sequence of monomer units) leading to conductivity is not needed.

We decided that the silica was causing the pigmented coatings to be inferior to the clear, so a small series of repeat formulations was run without the silica, and all subsequent work was done without silica. This series is given in Report 3/Table 3. In this series, the corrosion differences were too slight to discriminate between the blank and the additives. However, in the scribed area, differences were seen. Emeraldine base or another polyaniline (Neste) each gave a "good" appearance rating after 200 hours, versus a "poor" rating for the blank. Another experimental material, dianilinobenzoquinone, also was "good". Sicorin RZ, a commercial corrosion-inhibitory pigment, was poor as was the diacetate of benzoquinonedioxime diacetate.

The difference between these two sets of results show that caution must be used in comparing corrosion inhibitors; the results are formulation-dependent and test-dependent.

Synthesis of diacylated benzoquinonedioximes

Following up on the above-mentioned indication of activity with the dibenzoate of benzoquinonedioxime, we took advantage of the commercial availability of the benzoquinonedioxime (a rubber crosslinker made by Lord Corp.) and we synthesized the diacetate, the dioctanoate of benzoquinonedioxime as well as a polymer from hexamethylenediisocyanate and benzoquinonedioxime. The polymer was totally insoluble in all solvents tried.

Test series with soluble and insoluble additives

We tested at D/L Laboratories a series of additives to follow up on the activity seen in our first series. Where necessary, they were reprepared. Unlike the first test series, this series was done without silica since high loadings of solid additives appear to confuse the results when primers are being tested. This series was run as two subsets: soluble materials and dispersed insoluble materials. Versicon (a commercial polyaniline) and Drexel's N,N'-bis(4-aminophenyl)-p-benzoquinonediimine (so-called "trimer") were included in this set. All of these tests were run using an Akzo Nobel (Columbus, Ohio) supplied melamine resin-crosslinkable polyester. Steel plates were prepared not only for both D/L Laboratories salt fog testing but also for possible KSC EIS measurements. Glass slides with the same coatings were also prepared to be sent to Prof. Epstein's laboratory. Thus, we tried not only to compare materials but also test methodologies.

The results of this test series, presented in Report 4/Table 4, lent support to our original hypothesis; we found that small segments of polyaniline (exemplified by the Drexel "trimer") was active, also N,N'-diphenyl-p-phenylenediamine, a bis(long-chain-alkylamino)benzoquinone, and a quinonedioxime diester all exhibited anticorrosive action. The "trimer" seemed more active than the best of the polyanilines.

Methylenebis-p-toluidine had activity in protecting the scored area of the test plates but not the wide area covered by the coating. We may assume that it diffused out from the edges of the coating adjacent to the cut and thus protected the bare metal.

Another series was run in a urethane coating (obtained from Akzo Nobel, Troy, MI). In this series, Prof. Levon's various doped polyanilines were also compared but the results on these will not be reported here. Our results showed corrosion inhibitory activity equivalent to PANi (Versicon) with N,N'-diphenyl-p-phenylenediamine (Naugard J) and almost as good with the dibenzoate of benzoquinonedioxime. The scribed (bare) area was protected by Versicon, didodecylaminobenzoquinone, benzoquinonedioxime dioctanoate, and methylenebis-p-toluidine.

Attempted synthesis of quinonedioxime polyesters

Following up on the activity seen with diacylated benzoquinonedioximes, three quinonedioxime polyesters were made by reaction of quinonedioxime with several diisocyanates, but they were insoluble and thus could not be tested in the mode intended.

Concept and working hypothesis for further work on the project

Based on results up to this point, plus continued reading of the literature including Dr. B. Wessling's theories, it seemed to us that one way of interpreting the anticorrosive activity of polyaniline is that the active groups in it may be its quinonediimine groups and the reduced (phenylenediamine) part of the molecule may serve as a source for such groups, with oxygen of the air serving as the oxidant. The anticorrosive effect may come from passivation of the iron by formation of oxide of the proper morphology. Therefore, in general, polymers and non-polymer compounds with good bonding to steel with groups having reversible air-oxidation/iron-reduction chemistry at the proper emf may provide corrosion protection. The quinonedioxime group may be one example of a structure fitting this general requirement. Simple p-phenylenediamines and their quinoid oxidation products were thought also to fit this hypothesis.

Exploratory route for benzoquinonediimines from benzoquinone plus isocyanates

In our literature review of the N,N'-diphenyl-p-benzoquinonediimine we found a cursory and equivocal report (Staudinger and Endle 1917) of the formation of this compound from benzoquinone plus phenyl isocyanate. This unobvious reaction, if it could have been made to go in good yield, would have provided a novel entryway into a new class of polymers, having the electroactive quinonediimine ring built into a polyurethane coatings, for example. A preliminary hint that the reaction might go was a thin-layer chromatographic spot at the same point from the reaction of benzoquinone plus phenyl isocyanate as the known N,N'-diphenyl-p-benzoquinonediimine. On the other hand, this spot did not show the characteristic red color.

Staudinger's method using a sealed tube at high temperature was deemed unsafe, but to try to make the reaction practicable, we tried to find catalysts. Stannous octoate, a usual catalyst for additions to isocyanates, seemed not to accelerate the reaction, but triethylenediamine, also a known catalyst for isocyanate additions, did seem to accelerate the reaction judging by carbon dioxide evolution. The analysis of the products from this catalyzed run by FTIR shows bands matching those of the authentic diimine plus unreacted benzoquinone and a putative intermediate. A recent cursory report from Norway (Froyen 1993) of a triphenylarsenic oxide as specific catalyst for a particular type of isocyanate-quinone reaction was found and this candidate catalyst was obtained for trial. Unfortunately, it did not seem to work.

Follow-up on the small-molecule hypothesis by testing of p-phenylenediamines

Since the project was given a six-month extensionat this point, we began follow-up on the indications that small molecules representing segments out of polyaniline might be useful anticorrosive additives. We located a series of commercially produced N,N'-disubstituted-p-phenylenediamines (made by Flexsys for rubber antioxidants/antiozonants) and provided several of these to Akzo Nobel for their corrosion testing. We also began to study benzoquinonediimines made from the phenylenediamines. A literature review provided oxidation methods and we made N,N'-diphenyl-p-benzoquinonediimine in an amount sufficient for salt spray testing.

Testing at Ohio State and KSC

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A set of six glass plates with selected non-polymeric and oligomeric diamines has been sent to Prof. Epstein at OSU for testing as electroactive passivators on pure iron. Likewise, a set of most of our coated steel plates, the same compositions as tested in the salt spray chamber at D/L Laboratories, was sent to Kennedy Space Center for EIS measurements, which were done unfortunately under the misconception that the coatings were electroconductive. This vitiated the test results. Because of this, and some internal evidence of at least one data entry error, this data will not be presented here. Likewise, the OSU results were not believed to be meaningful, perhaps because our samples were not electroconductive, whereas the OSU methodology had been developed for polyaniline in the electroconductive form.

Further study of N,N'-disubstituted p-phenylenediamines and oxidation products thereof

We further pursued our strategy of making and testing small molecular weight analogs of polyaniline.We made N,N'-diphenyl-p-phenylenediimine successfully from N,N'-diphenyl-p-phenylenediamine (Naugard J) by chemical oxidation with benzoyl peroxide. After further review of the p-phenylenediamine and p-benzoquinonediimine literature, we decided to use the direct oxygen oxidation of the substituted phenylenediamines to make the desired oxidation products, comprising benzoquinonediimines, following a brief published report (Rotschova and Pospisil 1981).

We prepared a series of air-oxidation products of N,N'-disubstituted-p-phenylenediamines. In the case of N-(p-toluenesulfonamido)diphenylamine which resisted air oxidation, a crude PbO_2 oxidation product was made. Infrared spectra were run to characterize these products, which were for the most part mixtures, predominantly quinonediimines. These, along with the precursor diamines, were submitted for salt-spray 200-hour corrosion testing on steel plates in a cured polyester matrix, at D/L Laboratories. To recapitulate the rationale behind this work, these substances were considered non-polymeric models for both the oxidized (quinonediimine) and reduced (p-phenylenediamine) moieties of polyaniline.

Synthesis of N-carbamoyl-N'-phenyl-p-phenylenediamines

N-carbamoyl-N'-phenyl-p-phenylenediamines may be considered as models for the p-phenylenediamine segment of polyaniline with a moderately electron-withdrawing group on one of the nitrogen atoms. We did not find any of the simple compounds of this type in the literature. We did find a complex one with a monomer group on one end (Scholnik and Rajbenbach 1982).

For purposes of screening this type of structure for anticorrosion action, we made three N-carbamoyl-N'-phenyl-p-phenylenediamines (ureas). These were grayish crystalline sharp-melting solids (all in the 220-260C range) with infrared spectra consistent with the carbanilide structure. Nitrogen analyses confirmed the structure.

N-phenylcarbamoyl-N'-phenyl-p-phenylenediamine.
Anal. Calcd. for $C_{19}H_{17}N_3O$: N 13.86%. Found: N 13.87.

N,N'-4-methyl-1,3-phenylenebis(4-anilinophenylurea).
Anal. Calcd. for $C_{33}H_{30}N_6O_2$: N 15.49%. Found: N 15.41.

N,N'-hexamethylenebis(4-anilinophenylurea).
Anal. Calcd. for $C_{32}H_{36}N_6O_2$: N 15.67%. Found: N 15.52.

Subsequent to the project, they were given to Dr. P. Spellane at Akzo Nobel for testing. It should be noted that we consider this family of ureas from 4-aminodiphenylamine to be of general interest as anticorrosives and for other applications. Polymeric versions can be made using polyisocyanates, but time did not permit us to explore in this direction.

Comparative testing of N,N'-disubstituted-p-phenylenediamines and oxidized products

To complete the project, we ran salt-spray tests at D/L Laboratories on a series of air-oxidation or, in two cases, chemical-oxidation products of N,N'-disubstituted-p-phenylenediamines in comparison to their unoxidized precursors. The test medium was a melamine-formaldehyde-crosslinked polyester provided by Akzo Nobel (Columbus), which had been used heretofore in our project. The data is presented in Table 6.

Acetone wipes were used to eliminate those coatings which were not adequately cured. The p-phenylenediamines with N,N'-dialkyl groups were found to prevent the acid cure; their testing was aborted. Of the materials tested for 200 hours, the N,N'-diphenyl-p-phenylenediamine (Naugard J) and oxidation product N,N'-diphenyl-p-benzoquinonediimine were best (the oxidized product slightly better underfilm as well as in the scribed area). Other N-phenyl-p-phenylenediamines gave overall corrosion protection; their oxidation products did not. The best scribed area protection (distance damaged and blistering) was with oxidized p-(p-toluenesulfonamido)diphenylamine (Aranox); next best were Aranox and Naugard J themselves. This result makes further work quite practical because Aranox and Naugard J are commercial (Uniroyal) antioxidants. Aranox is not intensely colored, even after attempted air oxidation, so it does not have the staining problem that the Naugard J has. It was noted in earlier work at Stauffer Chemical (Jaffe and Toy 1972) that N-acylation can retard the oxidative degradation of p-phenylenediamines, so these observations encourage further work in coating applications of this family of p-phenylenediamine derivatives.

Prior art regarding p-phenylenediamines as corrosion inhibitors

To gain perspective on the possible novelty and patentability of the p-phenylenediamines as corrosion inhibitors, we did a literature search. Some patent references were found, notably the following: Cho *et al.* 1994 showing p-phenylenediamine and some substituted versions as corrosion inhibitors for lubricating oils for copper; Farng *et al.* 1990 showing some N,N'-disubstituted phenylenediamines as antioxidants and corrosion inhibitors for lubricants; Jaffe and Toy 1972 showing N-acyl-N,N'-dialkyl-p-phenylenediamines as antioxidants and corrosion inhibitors for oils; Kaiya *et al.* 1975 showing N-isopropyl-N'-phenyl-p-phenylenediamine in complex corrosion inhibitory coating, where it may be serving as antioxidant; Nikolova and Raichev 1982 showing N-isopropyl-N'-phenyl-p-phenylenediamine inhibiting iron corrosion in

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acid medium; Okazaki *et al.* 1993 showing m-phenylenediamine in corrosion-inhibitory epoxy coating; Phillips 1986 showing p-phenylenediamines in liquid fuels, maybe as antioxidants; Schachter and Lohonyai 1984 showing N-isopropyl-N'-phenyl-p-phenylenediamine as corrosion inhibitor for iron in aqueous HCl or sulfuric acid. There are probably many references on m-phenylenediamine in curing epoxy coatings. No reference was found that exactly anticipated the p-phenylenediamines as corrosion inhibitors in coatings. There are of course hundreds of references to the N,N'-disubstituted-p-phenylenediamines as antioxidants and antiozonants, especially for rubber where they have been used on a large scale for half a century. It should be noted that longer chain analogs of the phenylenediamines, with three or more phenylene rings, are within the program of Prof. Y. Wei at Drexel University.

Reaction products of the diglycidyl ether of bisphenol-A with p-aminodiphenylamine

Attempts to make an epoxy coating precursor from diglycidyl ether of bisphenol-A and 4-aminodiphenylamine, even at as high as 4:1 molar ratio of diepoxide to amine, gave hard cured products at about 90C. This unexpected result does suggest that 4-aminodiphenylamine might be used directly as part of the curing agent in epoxy coatings as a way to introduce a corrosion-inhibitory structure. A further motivation to do this is a perceived advantage of aromatic amine-cured epoxy coatings compared to aliphatic amine-cured epoxy coatings.

Final Project Findings and Recommendations

We believe that we have supported our initial belief that polyaniline is not a special corrosion inhibitor derived from its conjugated p-phenylenediamine/p-benzoquinonediimine structure, and also not on its ability to be electroconductive when doped. We found that the m-isomer which cannot be electroconductive also exhibits substantial corrosion inhibition activity, when compared to polyaniline (admittedly not in the best formulation; this comparison should be redone).

We also found that small segments of polyaniline, representing either the reduced (i.e. p-phenylenediamine) portion or the oxidized (i.e. p-benzoquinonediimine) portion can show corrosion inhibiting activity on steel.

In particular the corrosion inhibiting activity of the p-phenylenediamines is interesting especially since several of these are reasonably low cost articles of commerce, being made for use in rubber as antioxidants and antiozonants. The 4-amino-p-phenylenediamine is a low cost building block for rubber chemicals and thus offers itself as a building block also for corrosion inhibitors. It can be readily acylated and reacts readily with epoxy resins, isocyanates, etc., so should be easily incorporated into coatings.

The phenylenediamines may migrate out through a top coat with variable discoloration. Aside from the color problem, there are also toxicological/environmental/performance problems that can arise from migration of these diamines. There is one obvious way to avoid the problem - namely, to react the compounds into the coating resin. They could still discolor but at least they should stay in the primer layer. The color of polyaniline seems accepted (in this project at least) as long as it is in a primer layer.

An interesting question arises in regard to reacting the N,N'-di-substituted p-phenylenediamines reaction with epoxies. If these react in the normal fashion of an amine with an epoxy group, at least one nitrogen will now be fully substituted (i..e have no hydrogen atom left on it). Therefore, it is likely that these structures cannot so readily form the quinonediimine structure which may be the true active iron-passivating ingredient. The question has some practical significance as well as theoretical interest. One favorable possibility is that they may work as corrosion inhibitors but not discolor.

The shortcoming of the p-phenylenediamines is that most of them are "staining" compounds, i.e. they form highly colored oxidation products quite readily in air. The acyl version, exemplified by Aranox (N-p-toluenesulfonyl-N'-phenyl-p-phenylenediamine) is better in regard to color and color stability. Although it can be oxidized chemically to the quinonediimine (Sarul *et al.* 1982), we find it to be quite resistant to air oxidation. If these N-acyls work well as corrosion inhibitors, they probably are the preferred class of compounds from a stability and color viewpoint.

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Report 1 with Table 1

116 East 16th Street
New York, New York 10003   212-777-4445   212-505-8419 FAX

January 30, 1996

PolyTechnic University
Six Metrotech Center
Brooklyn, NY 11201

Att: **Dr. E&& D. Weil**
     Research Professor - Polymer Research Inst.

DL-10882

OBJECTIVE

To evaluate various pigments in a thermosetting polyester melamine coating.

PRODUCTS TESTED

The pigments and the resin binder solution were submitted by Polytechnic University and labeled as follows:

Pigments

Talc Micron 665, Montana

Talc Micron 665, Montana, PANI undoped (7.91%)
    10/19/72/S-1

Mica 221, Whittaker, Clark & Daniels

Mica 221, Whittaker, Clark & Daniels,
    Mica + ØPANI (7.93%) 10/24/73/S-1

Barium Sulphate Blanc Fixe F HU-VJ-8/07

Barium Sulphate Blanc Fixe F, Sachteleban Chemie,
    + PANI (Base) 8%, 11/6/78/S-1

Silica Siltex 44, Kapolite

Silica Siltex, Kapolite, PANI 7.78% (Base Form)

SICOR SPO

SICOR ZNP/S

PRODUCTS TESTED (cont)

Resin/Binder Solution

AKZO Nobel Flexiable Primer, Clear - 460,
November 22, 1995

PROCEDURE

The pigments were dispersed in the resin/binder solution, using a high speed Cowles disperser, at a pigment to binder solution ratio of 1:2. The resultant coatings were applied to cold rolled steel*: using a three mil Bird applicator, flashed off for fifteen minutes then baked at 325°F for twenty minutes. The coated panels were then exposed in a salt spray chamber in accordance with ASTM B 117. Upon completion of the exposure they were evaluate for corrosion resistance.

TEST METHODS

The test methods used in this study were:

Test	Method
Fineness of Dispersion	D 1210
Salt Spray (Fog) Resistance	B 117
Blister Evaluation	D 714
Rust Evaluation	D 610
Corrosion Evaluation Overall Area - Procedure B	D 1654

TEST RESULTS

The test results are shown in the Appendix.

* 1010 cold rolled, abrasively ground, wrapped in rust
Solvent cleaned. Purchased from Q-Panel (Cleveland)
Type S (0.032") (S36)   216-835-8700
                                                        Linda Colombo
                                                        Marty Jones

TEST RESULTS (cont)

Blistering was evaluated in accordance with ASTM D-714

Size		Frequency	
10	(No blisters)		
8	Very Small	F	- Few
6	Small	M	- Medium
4	Moderate	MD	- Medium Dense
2	Large	D	- Dense

Rusting was evaluated in accordance with ASTM D 610 as follows:

Rust Grade	Description
10	No rusting or less than 0.01% of surface rusted
9	Minute rusting, less than 0.03% of surface
8	Few isolated spots, less than 0.1% of surface
6	Extensive rusts spots, but less than 1% of area
4	Rusting to the extent of 10% of surface rusted
2	Approximately one third of surface rusted
0	Approximately 100% of surface rusted

Corrosion was evaluated in accordance with ASTM D 1654, Procedure B. The specimens were evaluated for corrosion spots, blisters or any other type of failure. The percent failed area and the corresponding ASTM rating were reported as follows:

Area of failure %	Rating Number
No failure	10
0 - 1	9
2 - 3	8
7 - 10	6
21 - 30	4
41 - 55	2
> 75	0

D/L Laboratories

Mario Lazaro
Group Leader

CW

cc: T. Sliva

Table I

TEST RESULTS	Clear Coating	Sicor SPO	Sicor ZNP/S	Talc Micron 665 Translucent	Talc Micron 665 PANI	Mica 221 Translucent	Mica 221 PANI	Barium Sulfate Translucent	Barium Sulfate PANI	Silica Siltex 44 Translucent	Silica Siltex 44 PANI
Fineness of Dispersion Hegman	NA	6	6	5.75	4.5	4.5	6 (a)	2	0	3.75	4
Film Appearance Color	Clear	Milky	Translucent	Translucent	Dark	Translucent	Dark	Translucent	Dark	Translucent	Dark
Integrity	Good	Good Sl. Orange Peel Film Mottling	Excellent	Excellent	Good Particles	Good Textured	Fair Rough	Good Sl. Rough	Good Very Rough	Excellent	Excellent
Salt Spray (Fog) Resistance											
Blistering ASTM 100 Hours	10	10	10	6F	10	8F	10	10	10	8F	10
200 Hours	8cl	8F	9F/8F	6F/6M	10	(b)	(b)	(b)	(b)	4M	8F
Rusting ASTM 100 Hours	10/9	10	10	10	8	10	0	0	8/9	10	10
200 Hours	10/9	10	10	9	6	(b)	(b)	(b)	(b)	10	9
Corrosion ASTM 100 Hours											
Overall Area – Method B Percent	0/4	0	0	28/54	5	5/28	100	100	2	54/21	0
Area of Failure ASTM Rating	10/8	10	10	4/2	7	7/4	0	0	8	2/4	10
200 Hours											
Overall Area – Method B Percent	66/59	7/14	15/52	33/66	85/81	(b)	(b)	(b)	(b)	100	22/26
Area of Failure ASTM Rating	1/1	6/5	5/2	3/1	0/0	(b)	(b)	(b)	(b)	0	4/4

Note: First panel/Second panel

(a) Pigment to binder ratio increased to 1:3, due to high viscosity at the 1:2 ratio.

(b) Exposure terminated after 100 hours.

CL – Clusters

116 East 16th Street
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Accredited by National Institute of Standards and Technology–No. 0252
Accepted by Canadian General Standards Board–No. 76005
ISO/IEC 25 Approved

March 19, 1996

PolyTechnic University
Six Metrotech Center
Brooklyn,   NY 11201

Att: **Dr. Edward D. Weil**
     Research Professor - Polymer Research Inst.

<u>DL-10957</u>

OBJECTIVE

To evaluate   various   pigments   in   a   thermosetting
polyester melamine coating.

PRODUCTS TESTED

The pigments   and   the   resin   binder   solution   were
submitted by Polytechnic University and labeled as follows:

Pigments

18Z thru 28Z

Resin/Binder Solution

AKZO Nobel Flexible Primer, Clear - 460,
November 22, 1995

PROCEDURE

The pigments   were   dispersed   in   the   resin/binder
solution, using a high speed Cowles disperser, at a pigment
to binder solution ratio of 1:2.   Pigment sample 28Z was a
silica pigment supplied without the active ingredient.   The
active ingredient was added to the resin binder solution to
achieve a percent pigment content of 92.2% silica and 7.8%
active ingredient.   The resultant coatings were applied to
cold rolled steel using a three mil Bird applicator, flash
off for fifteen minutes then baked at 325°F for twenty
minutes.   The coated panels were then exposed in a salt spray
chamber in accordance with ASTM B 117.   Upon completion of
the exposure they were evaluated for corrosion resistance.

TEST METHODS

The test methods used in this study were:

Test	Method
Fineness of Dispersion	D 1210
Salt Spray (Fog) Resistance	B 117
Blister Evaluation	D 714
Rust Evaluation	D 610
Corrosion Evaluation Overall Area - Procedure B	D 1654

TEST RESULTS

The test results are shown in the Appendix.

TEST RESULTS (cont)

Blistering was evaluated in accordance with ASTM D-714

Size	Frequency
10 (No blisters)	
8 Very Small	F - Few
6 Small	M - Medium
4 Moderate	MD - Medium Dense
2 Large	D - Dense

Rusting was evaluated in accordance with ASTM D 610 as follows:

Rust Grade	Description
10	No rusting or less than 0.01% of surface rusted
9	Minute rusting, less than 0.03% of surface
8	Few isolated spots, less than 0.1% of surface
6	Extensive rusts spots, but less than 1% of area
4	Rusting to the extent of 10% of surface rusted
2	Approximately one third of surface rusted
0	Approximately 100% of surface rusted

TEST RESULTS (cont)

Corrosion was evaluated in accordance with ASTM D 1654, Procedure B. The specimens were evaluated for corrosion spots, blisters or any other type of failure. The percent failed area and the corresponding ASTM rating were reported as follows:

Area of failure %	Rating Number
No failure	10
0 - 1	9
2 - 3	8
7 - 10	6
21 - 30	4
41 - 55	2
> 75	0

D/L Laboratories

Mario Lazaro
Group Leader

cw

cc: S. Spindel
    T. Sliva
    J. Gniecko

Table 2

APPENDIX

TEST RESULTS

		Clear Coating	18Z	19Z	20Z	21Z	22Z	23Z	24Z	25Z	26Z	27Z	28Z
Fineness of Dispersion	Hegman	NA	5½	5	6	5	5	5	4¾	5	4	5¾	3½
Film Appearance													
Color		Clear	Yellow	Black	Amber	Dk Brown	Translucent	Gray	Gray	Translucent	Translucent	Black	Lt Green
Integrity		Good	Excellent	Good	Excellent	Excellent	Excellent	Excellent	Excellent	Fair a	Excellent	Good	Good
Salt Spray (Fog) Resistance													
Blistering	ASTM												
100 Hours		10/cl	10/cl	10/8F	6F	10	10	8F	8F	8F/10	8F	8F	6M
200		8 cl	8MD/8M	8M	6M	8F	8F	6F	8F	8F/10	6M/6MD	6M	b
Rusting	ASTM												
100 Hours		10/9	10	10	10	10	10	10	9/10	9/10	10	10	6
200		9	10	9/10	10	10	10	10	9/10	9	6	10/9	b
		c	c				c	c			c		
Corrosion													
Overall Area – Method B													
100 Hours													
Area of Failure	Percent	0/15	22/2	8/5	3/10	0	0	3/10	3/8	3/0	3/0	3	100
ASTM	Rating	10/5	4/8	6/7	8/6	10	10	8/6	8/6	8/10	8/10	8	0
200 Hours													
Area of Failure	Percent	16	93	48	24	8/6	22/8	42/25	9	6/8	100	66	b
ASTM	Rating	(5)	0	2	4	(6/7)	(4/6)	2/4	(6)	(7/6)	0	1	b

← poor

a – Crystal–like appearance
b – Exposure terminated after 100 hours
c – Possible underfilm corrosion

cl = Cluster
Dk = Dark
Lt = Light

Page 4 of 4

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Accredited by National Institute of Standards and Technology–No. 0252
Accepted by Canadian General Standards Board–No. 76005
ISO/IEC 25 Approved

June 6, 1996

. PolyTechnic University
· Six Metrotech Center
Brooklyn, NY 11201

Att: Dr. Edward D. Weil
       Research Professor - Polymer Research Inst.

DL-11091

OBJECTIVE

To evaluate various pigments in a thermosetting polyester melamine coating.

PRODUCTS TESTED

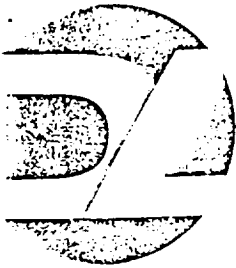The pigments and the resin binder solution were submitted by Polytechnic University and labeled as follows:

Pigments

10Z, 34Z, 40Z, 41Z and 45Z

Resin/Binder Solution

AKZO Nobel Flexible Primer, Clear - 460,

PROCEDURE

The pigments (1½ grams) were dispersed in 60 grams of resin/binder solution, using a high speed Cowles disperser. The resultant coatings were applied to cold rolled steel using a three mil Bird applicator and to a glass slide using a No. 70 wire wound rod applicator, flash off for fifteen minutes then baked at 325°F for twenty minutes. The coated steel panels were then exposed in a salt spray chamber in accordance with ASTM B 117. Upon completion of the exposure, they were evaluated for corrosion resistance. In addition, a blank coating contaning no pigment or additive was prepared.

TEST METHODS

The test methods used in this study were:

Test	Method
Fineness of Dispersion	D 1210
Salt Spray (Fog) Resistance	B 117
Blister Evaluation	D 714
Rust Evaluation	D 610
Corrosion Evaluation Overall Area - Procedure B	D 1654
Film Appearance	Visual

TEST RESULTS

The test results are shown in the Appendix.

Blistering was evaluated in accordance with ASTM D-714.

Size		Frequency	
10	(No blisters)		
8	Very Small	F	- Few
6	Small	M	- Medium
4	Moderate	MD	- Medium Dense
2	Large	D	- Dense

Rusting was evaluated in accordance with ASTM D 610 as follows:

Rust Grade	Description
10	No rusting or less than 0.01% of surface rusted
9	Minute rusting, less than 0.03% of surface
8	Few isolated spots, less than 0.1% of surface
6	Extensive rusts spots, but less than 1% of area
4	Rusting to the extent of 10% of surface rusted
2	Approximately one third of surface rusted
0	Approximately 100% of surface rusted

TEST RESULTS (cont)

Corrosion was evaluated in accordance with ASTM D 1654, Procedure B. The specimens were evaluated for corrosion spots, blisters or any other type of failure. The percent failed area and the corresponding ASTM rating were reported as follows:

Area of failure %	Rating Number
No failure	10
0 - 1	9
2 - 3	8
7 - 10	6
21 - 30	4
41 - 55	2
> 75	0

D/L Laboratories

Marie Lazaro
Group Leader

cw

cc: S. Spindel
    T. Sliva
    J. Gniecko

APPENDIX

Table 3

TEST RESULTS

	Dispersions	Blank	10Z	34Z	PAN (NCsH?) 40Z	Sicorin RZ 41Z	EB 45Z
Fineness of Dispersion	Hegman	NA	4½	5	1	6½	1
Film Appearance							
Color		Clear	Brown	Brown	Black	Clear	Black
Integrity		Excellent	Fair	Fair	Poor	Excellent	Poor
			a	a	a	b	a
Salt Spray (Fog) Resistance							
Blistering	ASTM						
100 Hours		9F/8F	10	10	10	8F/10	10
200 "		8F/6F	4F	8F/6F	8F	8F/6F	4F
		c	c	c		c	c
Rusting	ASTM						
100 Hours		9	10	9	10	10	10
200 "	No diff.?	9/8	8/9	8.	9	9	10
Corrosion							
Overall Area – Method B							
100 Hours							
Area of Failure	Percent	5	0	8	0	3/0	0
ASTM	Rating	7	10	6	10	8/10	10
200 Hours							
Area of Failure	Percent	20	26	26	15	15	15
ASTM	Rating No diff.?	5	4	4	5	5	5
Scribed Area							
100 Hours							
General Appearance		Good	Excellent	Fair	Good	Fair	Good
Affected Area							
Distance from scribe	mm	3	1	5	2	8	2
Blistering	ASTM	8M	10	8MD	8F/6F	6M	8F
200 Hours							
General Appearance		Poor	Good	Poor	Good	Poor	Good
Affected Area							
Distance from scribe	mm	12	2	11	3	18	2
Blistering	ASTM	6MD	4F	2F/4M	4F	6MD	6F

First Panel/Second Panel
a – Particles
b – Haze
c – Defect at bottom portion of test panel

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Accredited by National Institute of Standards and Technology–No. 0252
Accepted by Canadian General Standards Board–No. 76005
ISO/IEC 25 Approved

June 3, 1996

Report 4/Table 4

- PolyTechnic University
- Six Metrotech Center
Brooklyn, NY 11201

Att: Dr. Edward D. Weil
      Research Professor - Polymer Research Inst.

DL-11076

OBJECTIVE

To evaluate various pigments in a thermosetting polyester melamine coating.

PRODUCTS TESTED

The pigments and the resin binder solution were submitted by Polytechnic University and labeled as follows:

Pigments

7/8Z, 35Z, 37Z, 42Z, 43Z, 44Z, 46Z and 47Z

Resin/Binder Solution

AKZO Nobel Flexible Primer, Clear - 460,

PROCEDURE

The pigments (1 ½ grams) were dispersed in 60 grams of resin/binder solution, using a high speed Cowles disperser. The resultant coatings were applied to cold rolled steel using a three mil Bird applicator and to a glass slide using a No. 70 wire wound rod applicator, flash off for fifteen minutes then baked at 325°F for twenty minutes. The coated steel panels were then exposed in a salt spray chamber in accordance with ASTM B 117. Upon completion of the exposure, they were evaluated for corrosion resistance.

Polyester resin binder

APPENDIX

Table 4
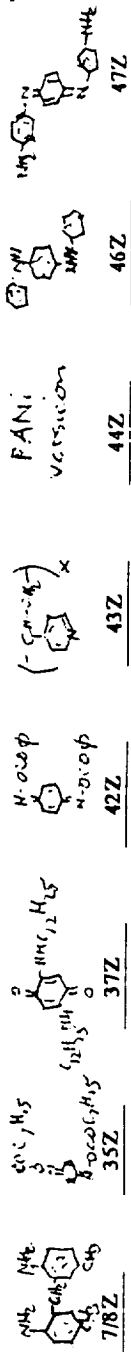
TEST RESULTS		Blank	7/8Z	35Z	37Z	42Z	43Z	44Z (FANI version)	46Z	47Z
Fineness of Dispersion	Hegman	—	7½	7½	7½	6	4	7½	7½	2
Film Appearance										
Color		Clear	Clear	Clear	Carmel	Clear	Clear	Green	Clear	Black
Integrity		Excellent	Excellent	Good	Excellent	Fair	Poor	Poor	Good	Poor
						a	(c)	a	b	b,c
Salt Spray (Fog) Resistance										
Blistering										
100 Hours	ASTM	9F/8F	10	10	9cl	10	8F	10	10	10
200 "		8F/6F	10/8F	8cl/8F	8cl	8cl/8F	4M/2F	10/8F	9cl	10
Rusting										
100 Hours	ASTM	9	9/8	9	9/10	9	4	10/9	9	9
200 "		9/8	(8/6)	(8)	(9)	(9)	4	(9)	(9)	(9)
Corrosion										
Overall Area – Method B										
100 Hours										
Area of Failure	Percent	5	8	8	2	2	90	1	4	2
	Rating ASTM	7	6	6	8	8	0	9	8	8
200 Hours										
Area of Failure	Percent	20	45	(12)	9	(16)	100	7	(15)	(6)
	Rating ASTM	5	2 BAD	(5)	6	(5)	0 BAD	6	(5)	7
Scribed Area										
100 Hours										
General Appearance			(Excellent)	Good	Good	(Excellent)	Fair	(Excellent)	Good	Good
Affected Area										
Distance from scribe	mm ASTM	3 / 8M	2	8	6	1	8	1	2	4
Blistering	ASTM		(10)	8F	8M	(10)	8F	(10)	8F	(10)
200 Hours										
General Appearance		Poor	(Good)	Poor	Fair	Fair	Poor	(Good)	(Good)	(Good)
Affected Area										
Distance from scribe	mm ASTM	12	7	15	16	15	11	10	8	6
Blistering	ASTM	(8 MD)	(10)	2F	4M	4M	2F	(6M)	(6MD)	(10)

First Panel/Second Panel

a – Bénard cells
b – Orange peel
c – Particles
d – Cluster of blister size indicated

Report 5/Table 5

June 3, 1996

· PolyTechnic University
· Six Metrotech Center
Brooklyn, NY 11201

Att: Dr. Kalle Levon
       Chairman - Dept of Chemical Eng.
       Chemistry and Materials Science

DL-11077

OBJECTIVE

To evaluate various thermosetting coatings.

PRODUCTS TESTED

The coating solutions were submitted by Polytechnic University and labeled as follows:

Two Component Coatings

7 + 8-Z, 34-Z, 35-Z, 37-Z, 42-Z, 43-Z, 44-Z, 46-Z
CC, KY21, XT1 and XT5

One Component Coatings (Ready to use)

P-21, P-25, P-29, P-31, P-35 and P-39

PROCEDURE

The two component coatings were mixed together as supplied. These mixtures were applied to cold rolled steel using a three mil Bird applicator and to a glass slide using a No. 70 wire wound rod applicator. The solvent was allowed to flash off for fifteen minutes then the coating was baked at 88°C (190°F) for sixty minutes. The coated steel panels were then exposed in a salt spray chamber in accordance with ASTM B 117. Upon completion of the exposure they were evaluated for corrosion resistance.

TEST METHODS

The test methods used in this study were:

Test	Method
Salt Spray (Fog) Resistance	B 117
Blister Evaluation	D 714
Rust Evaluation	D 610
Corrosion Evaluation Overall Area - Procedure B	D 1654
Film Appearance	Visual

TEST RESULTS

The test results are shown in the Appendix.

Blistering was evaluated in accordance with ASTM D-714

Size
10 (No blisters)
8 Very Small
6 Small
4 Moderate
2 Large

Frequency

F - Few
M - Medium
MD - Medium Dense
D - Dense

Rusting was evaluated in accordance with ASTM D 610 as follows:

Rust Grade	Description
10	No rusting or less than 0.01% of surface rusted
9	Minute rusting, less than 0.03% of surface
8	Few isolated spots, less than 0.1% of surface
6	Extensive rusts spots, but less than 1% of area
4	Rusting to the extent of 10% of surface rusted
2	Approximately one third of surface rusted
0	Approximately 100% of surface rusted

TEST RESULTS (cont)

Corrosion was evaluated in accordance with ASTM D 1654, Procedure B. The specimens were evaluated for corrosion spots, blisters or any other type of failure. The percent failed area and the corresponding ASTM rating were reported as follows:

Area of failure %	Rating Number
No failure	10
0 - 1	9
2 - 3	8
7 - 10	6
21 - 30	4
41 - 55	2
> 75	0

D/L Laboratories

Mario Lazaro
Group Leader

cw

cc: S. Spindel
    T. Sliva
    J. Gniecko

Table 5

APPENDIX
URETHANE

TEST RESULTS	IN SOLN	7+8-Z	34-Z	35-Z	37-Z	42-Z	43-Z	44-Z	46-Z	CC	KY21	XT-1	XT-5	P-21	P-25	P-29	P-31	P-35	P-39
Fineness of Dispersion	Mils	1.7	1.7	1.6	1.9	1.7	1.6	1.7	1.7	1.6	2.0	1.7	1.2	1.9	2.0	2.0	a	a	a
Film Appearance Color		Clear	Clear	Clear	Brown	Clear	Clear	Clear	Clear	Clear	Green	Clear	Clear	Clear	Blue	Blue	Clear	Clear	Clear
Integrity		Excellent	Poor	Excellent	Good	Fair	Poor	Excellent	Excellent	Excellent	Poor	Excellent	Excellent	Excellent	Excellent	Excellent	a	a	Clear
			c		b,c	b	c	b	b	b	c				b	b			
Salt Spray (Fog) Resistance																			
Blistering 100 Hours	ASTM	10	9cl	9cl	9cl	9cl/10	9cl	10	10	10/9cl	10	9cl	8P	10	10	10	–	–	–
200 "		10	9cl	9cl	8cl	9cl/10	6F	10	10	10/4cl	10	8cl	8F	8F/10	10	10	–	–	–
Rusting 100 Hours	ASTM	9	8/9	9	9	9/10	8/9	10	10	10/9	8/9	9	8/9	9	8	8/4	–	–	–
200 "		9	8/9	9	9	9/10	6	10	10	10/9	8	8/9	8	8	6	2	–	–	–
Corrosion Overall Area – Method B																			
100 Hour Area of Failure	Percent	4	8	5	4	8/0	12	0	0	0/8	13/5	8	13	3	10	42	–	–	–
ASTM	Rating	8	6	7	8	6/10	5	10	10	10/6	5/7	6	5	8	6	3	–	–	–
240 Hour Area of Failure	Percent	5	12	10	6	5/0	90	0	0	0/8	26	7	10	16	76	100	–	–	–
ASTM	Rating	7	5	6	7	(7/10)	0	(10)	(10)	10/6	4	6	6	5	0	0	–	–	–
Scribed Area																			
100 Hour General Appearance		Good	Good	Good	Good	Good	Fair	Good	Good	Excellent	Good	Fair	Good	Good	Good	Good	–	–	–
Affected Area Distance from scribe	mm	10	8	10	10	10	12	11	10	9	10	9	8	4	5	4	–	–	–
Blistering	ASTM	8M	8M	8M	9M	8M	6F	8M	9M	8M/9M	8F	8M	8M	10	10	10	–	–	–
200 Hour General Appearance		(Good)	Poor	(Good)	(Good)	Fair	Poor	(Good)	(Good)	Good	Fair	Good	Good	Fair	Poor?	Very Poor	–	–	–
Affected Area Distance from scribe	mm	12	13	13	12	10	15	10	10	12	17	11	13	11	4	4	–	–	–
Blistering	ASTM	8M	2F	6F/4F	8M	4F	6M	6F	4F	4F/6P	10	4F	4F	6F	10	d	–	–	–

First Panel/Second Panel
cl – Cluster of blisters ite indicated
a – No cure

b – Orange peel
c – Particles

d – Extensive rusting at affected scribed area

116 East 16th Street
New York, New York 10003   **212-777-4445**   **212-505-8419 FAX**

December 26, 1996

PolyTechnic University
Six Metrotech Center
Brooklyn, NY 11201

Att: **Dr. Edward D. Weil**
      Research Professor - Polymer Research Inst.

DL-11323

OBJECTIVE

To evaluate various pigments in a thermosetting polyester melamine coating.

PRODUCTS TESTED

The pigments and the resin binder solution were submitted by Polytechnic University and labeled as follows:

Pigments

1-7R-8, 1-7R-8SM, 1-9R-10, 1-9R-10SM, 1-11R-12, 1-11R-12SM,
1-16R-16, 1-16R-16SM, 1-19R-19, 1-19R-19SM, 61-Z and 61-ZSM

Resin/Binder Solution

AKZO Nobel Flexible Primer, Clear - 460,

PROCEDURE

The pigments (1 ½ grams) were dispersed in 60 grams of resin/binder solution, using a high speed Cowles disperser. The resultant coatings were applied to cold rolled steel using a three mil Bird applicator, flashed off for fifteen minutes then baked at 325°F for twenty minutes. The coated steel panels were then scribed with a large X and exposed in a salt spray chamber in accordance with ASTM B 117. Upon completion of 100 hours and 200 hours of exposure, the panels were evaluated for corrosion resistance. In addition, a blank coating contaning no pigment or additive was prepared and exposed.

TEST METHODS

The test methods used in this study were:

Test	Method
Fineness of Dispersion	D 1210
Salt Spray (Fog) Resistance	B 117
Blister Evaluation	D 714 ·
Rust Evaluation	D 610
Corrosion Evaluation	ASTM Scoring Scheme
Film Appearance	Visual

TEST RESULTS

The test results are shown in the Appendix.

Blistering was evaluated in accordance with ASTM D-714.

Size	Frequency
10 (No blisters)	
8 Very Small	F - Few
6 Small	M - Medium
4 Moderate	MD - Medium Dense
2 Large	D - Dense

Rusting was evaluated in accordance with ASTM D 610 as follows:

Rust Grade	Description
10	No rusting or less than 0.01% of surface rusted
9	Minute rusting, less than 0.03% of surface
8	Few isolated spots, less than 0.1% of surface
6	Extensive rusts spots, but less than 1% of area
4	Rusting to the extent of 10% of surface rusted
2	Approximately one third of surface rusted
0	Approximately 100% of surface rusted

Att: Dr. Ed Weil
Re: DL-11323

Table 6

APPENDIX

TEST RESULTS — Pigment/Binder ---->		Blank	8 (1-7R)	8SM	10 (1-9R)	10SM	12 (1-11R)	12SM	16 (1-16R)	16SM	19 (1-19R)	19SM	Z (61)	ZSM
FINENESS OF DISPERSION	Hegman	NA	7½	7½	7½	7½	7½	7½	7½	7½	0	7½	0	2½
DRY FILM THICKNESS	Mils	1.5	1.4	1.3	1.4	1.4	1.5	1.5	1.5	1.5	1.5	1.5	1.6	1.5
FILM APPEARANCE Color		Clear	Dk Brown	Dk Amber	Med Brown	Lt Brown	Black Olive	Amber	Black	Amber	Clear	Clear	Clear	Clear
Integrity		Excellent	Fair	Poor	Excellent	Excellent	Fair	Excellent	Fair	Excellent	Poor	Excellent	Poor	Excellent
MEK Rubs		100+	3 Reject	25 Reject	3 Reject	25 Reject	45 Reject	100+ Accept	3 Reject	100+ Accept	65 Borderline	100+ Accept	100+ Accept	100+ Accept
SALT SPRAY (FOG) RESISTANCE														
Blistering 100 Hours	ASTM	10	h	10	10	10	10	10	10	10	10	10	10	10
Blistering 200 Hours		10	*	*	*	*	*	8F	*	8F	6M	8F	(10)	(10)
Rusting 100 Hours	ASTM	10	0	10	10	10	10	10	10	10	10	10	10	10
Rusting 200 Hours		10	*	*	*	*	*	10	*	10	10	10	10	10
CORROSION														
Overall Area – Method B 100 Hours	Score	10	g	10	g	10	10	10	0g	10	10	10	10	10
200 Hours		10	*	*	*	*	*	(8)	*	(8)	6	(8)	(10)	(10)
Underfilm Corrosion 100 Hours		10	g	10	g	10	10	10	g	10	8	10	10	10
200 Hours		9	*	*	*	*	*	(9)	*	(9)	4	(9)	10	(9)
Scribed Area 100 Hours General Appearance		Good	Poor	Good	Fair	Good	Good	Good	Good	Good	Good	Good	Fair	Good
Affected Area Distance from scribe	mm ASTM	5	30	4	5	4	3	4	1-2	5	(1-2)	4	5	5
Blistering	ASTM	8D	9	8MD	9	8MD	8D	8D	9	8D	10	8D	8D	6D
200 Hours General Appearance		Fair	*	*	*	*	*	(Fair)	*	(Fair)	(Fair)	(Good)	Poor	Fair
Affected Area Distance from scribe	mm ASTM	11	*	*	*	*	*	12	*	12	(1-2)	9	11	11
Blistering	ASTM	4MD	*	*	*	*	*	8D	*	8D	6-4M	6D	4M	6D

* – Salt spray exposure terminated after 100 hours
a – Particles
b – Craters
c – Convection cells
d – Orange peel
e – Mottling
f – Very large particles
g – Coating exhibits erosion
h – Severe corrosion

Technical Report

New Anticorrosive Coatings with Polyaniline and Related Electroactive Groups

Profs E.D.Weil and Indra K.Varma

Report Period: July 1,1995 to Nov.30, 1995

Grantee Institution: Polytechnic University, Brooklyn, N.Y.

Table of Contents

1. Introduction

The main objective in the present investigation was to evaluate the structural requirements of electroactive polymers such as polyaniline for the corrosion protection of mild steel.

The corrosion of metals is an electrochemical process. Application of a positive potential within a certain given range and characteristic of the metal or its alloy has been successfully used for the protection of corrosion in some metals. Formation of a protective oxide layer by the electrochemical processes described below are responsible for passivation of mild steel and protects it from further corrosion.

$$x\ Fe \longrightarrow x\ Fe^{+p} + xp\ e^-$$

$$x\ Fe^{+p} + H_2O \xrightarrow{excess} Fe_x O_y + (xp)\ H^+$$
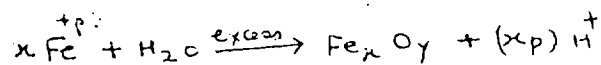
If a conducting polymer oxidised to a potential falling in the passivation range of the metal is painted on the surface of the metal it is expected to protect it from the corrosion.

$$Polymer + (xp) H^+ + xp\ e^- \longrightarrow \left(polymer\ H\ _{xp}\right)^0$$
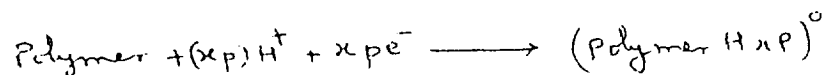
The polymer film is also expected to function indefinitely if the reduced form of the polymer can be oxidised by the air. If, however the polymer is not regenerated in its oxidised form, then it will function as a sacrificial film as in case of cathodic protection of Fe by Zn.

Polyanilines constitute a large class of conducting polymers which are formed by the chemical or electrochemical oxidative polymerization of aniline or substituted anilines. The terms leucoemeraldine, emeraldine and pernigraniline have been used to describe the different oxidation state of the polymer.
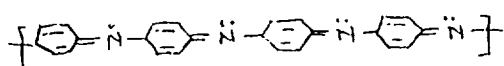

$$\sigma \approx 10^{-10}\ s\ cm^{-1}$$

Leuccemeraldine (LE)

$$\sigma \approx 10^{-10}\ s\ cm^{-1}$$
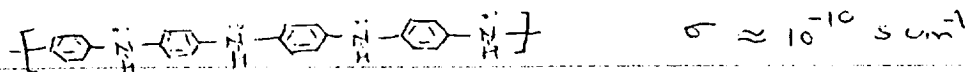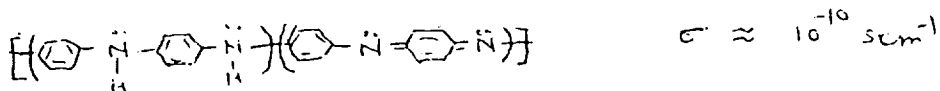
Emeraldine Base (undoped PANi)

$$\sigma \approx 1-5\ s\ cm^{-1}$$
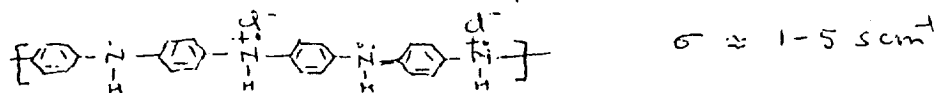
Emeraldine Hydrochloride (doped PANi.) (ES)

Pernigraniline

The imine nitrogen atoms can be protonated in whole or in part to give the corresponding salts. The degree of protonation depends on the oxidation state of the polymer and on the pH of the aqueous acid.

Complete protonation of the imine nitrogen atoms in emeraldine base results in the formation of a delocalised polysemi-quinone radical cation and is accompanied by an increase in conductivity by a 9 to 10 order of magnitude. Emeraldine base or salt may be useful in corrosion protection of Fe due to their various possible oxidation states .

The anodic synthesis of polyaniline(PANi) coatings and their assessment for protecting corrosion onto Fe sheets was reported as early as 1981 by Mengoli et.al.DeBerry in 1985 showed that stainless steels 410 and 430 may be protected from corrosion over extended periods by a film of polyaniline electrochemically deposited on the surface of steel. The corrosion protection of stainless steel (coated with PANi) in a solution of $0.1MH_2SO_4 + 0.1MNaCl + 0.15MNa_2SO_4$ has also been reported by MacDiarmid et al (1987).

Sathyanarayan(1992) reported that poly(ethoxy aniline) was eight times more effective than aniline in inhibiting corrosion of iron in 1N HCl . Polyaniline coating on mild steel is also effective in 3.5% saline solution (Thompson et al, 1994). Wessling et al (1994,1995) reported that mild steel, stainless steel and copper are passivated by a coating of PANi followed by an epoxy barrier paint. The corrosion rates were two times less in 3.5 % NaCl and 100 times less in 0.1N HCl. The level of corrosion protection provided by doped PANi to steel exposed to dil HCl was surprising. Zasty and Epstein (1995) observed that emeraldine base form of PANi passivates surface of Fe with a thin oxide layer. Zipperling Kessler and Co has recently announced PANi based preventive corrosion primer (CORRPASSIVE) with an epoxy top coat , and CORREPAIR for repairing rusted metal plates. The passivation reaction responsible for the amazing corrosion protection performance of PANi has been attributed to the redox catalytic properties of PANi . It oxidises iron to Fe2+ and itself reduced to leucoemeraldine. Oxygen further reoxidises the leuco form of PANi to the emeraldine salt.

Inspite of the published literature cited above, there are several aspects of corrosion protection aspect of PANi which need attention. No comparative evaluation of PANi coatings with the state-of-the-art materials has been reported. Troch and Nageli(1992) and Sekine et al (1992) observed very little corrosion protection of mild steel by the use of electrochemically deposited PANi film. Polyamines have been used as pickling inhibitors and it is quite possible that in PANi similar type of mechanism may be operative. Hence there is a need to assess related polymers devoid of quinone rings for corrosion protection. Michael addition reaction of aromatic and aliphatic amines with the quinoid rings of PANi may provide new materials with unique properties .Instead of using a 100% PANi as primer, it would be worthwhile to evaluate PANi coatings on corrosion inhibitors or PANi dispersions on inert carriers such as talc, mica, silica or $BaSO_4$.

Therefore in the present studies attention was given to following aspects;

1. Preparation, characterisation and reactions of PANi
2. Preparation of poly(m-aniline)
3. Polymerization of aniline in presence of inert carriers
4. Coating of corrosion inhibitors with PANi
5. Preliminary testing of corrosion

2. Preparation, Cl aracterisation and Reactions of PANi

The oxidation polyme rization of aniline (Aldrich) in 1N HCl (aqueous solution) using ammonium persulfate (Aldrich) as an oxidant was carried out both at room temperature as well as at low temperature (<5°C). The reaction scheme is given in eq.1

$$\text{①-NH}_2^+ \; S_2O_8^{2-} \xrightarrow{\quad\text{aq.acid}\quad} 2SO_4^{2-} \; + 2H^+ \; + \; \text{{①-NH}}$$
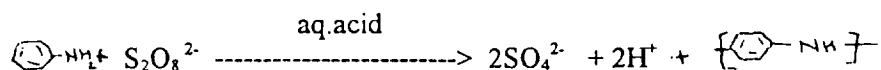
This indicates that oxidant is consumed stoichiometrically. However, detailed studies on polymerisation of aniline have revealed that oxidation of aniline by persulfate is a much slower process than oxidation by polyaniline in high oxidation state.In the major propagation step, polyaniline in the pernigraniline oxidation state acts as an intermediate for the oxidation of aniline. The reactive polymer species is believed to be a nitrenium ion which performs an electrophilic attack on aniline monomer. The selective oxidation of aniline by polymer and subsequent incorporation into the growing polymer chain represents an unusual class of addition polymerization. Since the oxidation product is polyaniline itself, an autoacceleration in the reaction kinetics is observed. The rate behaviour is described by

$$d[An]/dt \; = \; k'[An] + k''[An]\,[PANi]$$

where k' and k'' are rate constants for the formation of PANi in the absence and presence of PANi. k'' is found to be 2 to 4 orders of magnitude larger than k' for heterogeneous solution polymerization.

A variation in the oxidant to monomer ratio has been reported to influence the % yield of the polymer. Therefore, in the present work oxidant to monomer (O:M) ratio was varied to study the effect of reaction variables on % conversion. Typical reaction scheme for synthesis of PANi using O:M ratio of 1:4 and 1.5:1 is described below.

2.1 Preparation of PANi

a) Synthesis of PANi using a O:M ratio of 1:4
Aniline (14.88g) was dissolved in 100 mL of 1N HCl and solution cooled in an ice bath. Ammonium persulphate (9.12 g) was dissolved separately in 100 mL 1N HCl and this solution was also cooled in an ice bath.When the reactant temperature was below 5 $^\circ$C then the oxidant solution was added gradually to a well stirred solution of aniline. The temperature was maintained below 5 $^\circ$C during the addition. The dark green precipitates of PANi were obtained after few minutes and solution was maintained at low temperature for one hour. The solution was then stirred at room temperature for 2.5 h. The precipitates of PANi salt thus obtained,were washed with 0.5 L 1N HCl, distilled water (1L) and 0.1N NH$_4$OH (0.5L). The polymer was left overnight in 0.5L of 0.1 N NH$_4$OH. It was then filtered, washed with 0.1NH$_4$OH (250 mL) , distilled water and dried under dynamic vacuum for few days and then in an air oven at 80°C for 4h. Undoped PANi samples 7/21/57/S-1 and 7/31/61/S-1were prepared in yields ranging from 19-23 %. These yields are based on the amount of aniline taken in the initial feed.

b) Synthesis of PANi using an oxidant : monomer ratio of 1.5:1
Aniline (7.44g) in 200 mL of 1.2N HCl was stirred at room temperature and 27.2 g of ammonium persulfate in 200 mL of 1.2N HCl was added dropwise to the well stirred solution of aniline. Dark green precipitates of PANi were obtained within few minutes of stirring . The reaction solution was then stirred at room temperature overnight > 18h. Precipitates of PANi were collected by

filtration, washed with 0.5L of 1.2N HCl and 200 mL of deionised water. The PANI salt thus obtained was dried in a similar way as described in (a) above.

The yield of doped PANi sample 7/27/58/S-1 and 7/20/56/S-1 was in the range of 55-58%.

2.2 Characterisation of PANi

In the FTIR spectrum of undoped PANi quinoid and benzenoid ring absorptions were observed at 1586 and 1497 cm^{-1} respectively. The absorption band at 1307 cm^{-1} is due to C-N stretch of secondary aromatic amine. The C-H in-plane bending absorption was observed at 1165 cm^{-1} and the absorption peak at 831 cm^{-1} is characteristic of 1,4-disubstitued aromatic ring. (Fig 1).

In the TG trace of undoped PANi, recorded in nitrogen atmosphere an initial weight loss below 150 °C was observed due to loss of absorbed moisture. The major weight loss was above 364°C and 48 % weight loss was observed upto 674°C. The char residue at 800°C was ≈ 45 %. In case of doped PANi, additional weight loss step due to evaporation of dopoant molecules (HCl) was observed (Fig 2,3). The % char yield of doped PANI was less than the undoped sample. The thermal stability of PANi also depended on the method of preparation and higher char yields were obtained when O:M ratio was higher.

2.3 Reactions of PANi

The curing of general purpose epoxy resin (DER 331, epoxy eq. 189) (DOW Chem. Co.) with doped as well as undoped PANi was investigated. No gelation was observed when these samples were heated in an air oven at 80°C for several hours. Since PANi is insoluble in epoxy resins therefore , DBSA doped (dodecyl benzene sulfonic acid)PANi was dissolved in toluene and used for curing of epoxy resin. After thoroughly mixing the PANi solution and epoxy resin, the solvent was evaporated and curing reaction was monitored by DSC as well by heating in an air oven . No exothermic transition in DSC scan , indicative of curing reaction was observed.(Fig.4).

The nucleophilic addition reaction of aliphatic amine, such as diethylene triamine (DETA) with the quinone ring of PANi (undoped) was investigated in NMP solution at different temperatures. A deep blue solution was obtained when DETA was added to PANi in NMP but in the ir spectrum of the reaction product no additional absorptions due to aliphatic CH groups were observed. (Fig.5). The reaction was done at 75, 100 as well as 165°C with no success. Reaction of PANi with DETA in absence of solvent was also attempted with no success.

3. Preparation of poly (m-aniline)

The ammonolysis reaction of m-bromoaniline (Ullman reaction) was used for the synthesis of poly (m-aniline) (Ito et al,Macromolecules,28,5618, 1995).In a 100 mL three necked round bottomed flask equipped with a nitrogen gas inlet, a thermometer and a reflux condenser 10.35g of m-bromoaniline 4.23g of potassium carbonate and copper iodide (0.35g) were placed. Nitrobenzene (45 mL) was used as the solvent. The reactants were stirred at room temperature for 30 min. and nitrogen was passed.The temperature was raised to 210°C . The initial inhomogeneous yellow

solution turned orange around 140°C and finally turnd dark brown at 210°C. The reaction was carried for 24 h at 210°C. The contents were then cooled to room temp. and n-heptane was added to dissolve oligomers. After filtration. the residue was washed with methanol and 6N HCl several times to dissolve catalyst. Finally the residue was washed with methanol and dried in vacuum   (% yield = 50). Small quantity of the residue was also treated with 0.5N NH₄OH to prepare the neutral form.

In the ir spectrum of the polymer absorption peaks were present at 1590, 1485, 1307 and 709 cm^{-1}. The absorptions due to quinone (C=C and C=N) at 1590 and benzene skeleton (1485 cm^{-1}) and C-N stretching (1307 cm^{-1}) are similar to those observed in PANi and reported earlier in poly(m-aniline)(see Yoshizawa,K., Tanaka,K., Yamabe, T., Chem.Lett.,1311-1314, 1990; Tanaka,K., Yoshizawa, K., Takata, A., Yamabe,T., Yamauchi,J., Synth. Met., 43, 3297, 1991).There is, however, a difference in C-H out-of plane deformation mode in PANi and poly (m-aniline). In the ir spectrum of polyaniline, absorption at 831 cm^{-1} was observed which is characteristic of 1,4-disubstituted aromatic ring. This absorption band was absent in poly(m-aniline). An absorption peak was present at 709 cm^{-1} which may be due to C-H out-of- plane deformation of m- linkage. In the ir spectra of n-alkyl substituted poly(m-aniline)s two absorption peaks at 750 and 700 cm^{-1} have been reported due to 1,2,4-substitution. The literature value associated with m-linkage are 840,770 and 685 cm^{-1} .However these bands of polysubstitued benzenes do not have high enough accuracy for the assignment.
Poly(m-aniline can exist in (a) neutral, (b) salt, (c) cationic and (d) dehydrogenated forms

(a) neutral   (b) salt   (c)   (d) dehydrogenated
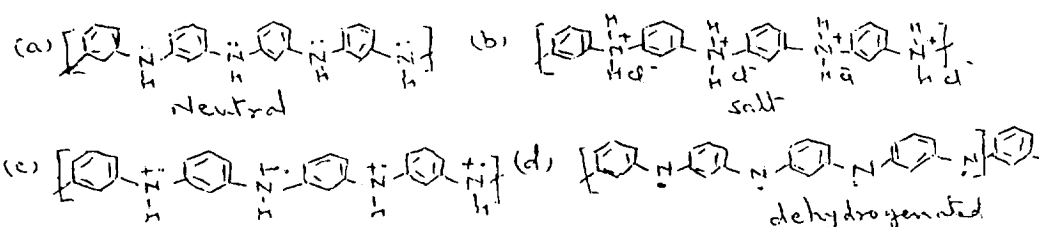
The cationic and dehydrogenated forms have unpaired electrons. Since the reaction was carried out in nitrobenzene at elevated temperature, therefore , the possibility of other side reactions can not be ruled out. Also Ullman reaction is believed to proceed by the coupling of the free radicals generated at relatively high temperature, therefore, the possibility of rearrangement to p- position can not be ruled out.The presence of m-linkage in polyaniline prepared by ammonolysis of p-bromoaniline has been repored earlier(Yoshizawa, K., Ito, A., Tanaka, K., Yamabe, T., Synth.Met., 48, 271, 1992).
Therefore, on the basis of ir it is not possible to assign the structure of poly(m-aniline) unambiguously.
The TG trace of neutral and doped polymer showed an unusually high char yield at 800°C in nitrogen atmosphere (Fig 6,7). These char yields are higher than those of polyaniline. The polymer was insoluble in most organic solvents.

4. Polymerization of aniline in presence of inert carriers

4.1 Materials

- Talc, Nicron 665 (Montanna Co.), specifications- % talc 99, Hegman fineness 6.1%, dry brightness-89.3%, oil absorption 45g/100g.
- Silica,Siltex 44 (Kaopolite Inc.)
- Barium sulfate ,Blanc Fixe F (Sackteleben Chemie)
- Mica ,Mica 221 (Whittaker, Clark and Daniels Inc.)
- Modified Mica, HiMod 270 SME (KMG Minerals)

Samples with different loadings of PANi were prepared by taking different quantities of aniline:oxidant while keeping the inert carrier quantity constant. The O:M ratio was 1:4 in all cases.

4.2 Reaction Conditions

Details of the reaction conditions for obtaining a PANi loading of 7.5% are described below. Aniline (15 ± 0.5 g) was dissolved in 200 mL 0f 1N HCl and 40 g of inert carrier was added. The resulting mixture was placed in an ice bath and stirred at low temp. for 30 min. Ammonium persulfate (9.58g) dissolved in 100 mL 1N HCl was also cooled in ice. The oxidant solution was then added slowly to a well stirred solution of aniline. The temp. was kept below 5°C. Total time for addition was 10-25 min. The dark green precipitates of PANi appeared after few min. The contents were stirred at low temp. for 1h and then at room temp. for 2.5h.After filtration,the residue was washed with 750 mL of 1N HCl, and 750 mL of deionised water. A small quantity of the residue was separated at this stage and consitutes the doped PANi on the inert carrier.Remaining residue was washed with 750 mL of 0.1N NH_4OH and then stirred with 500 mL of 0.1N NH_4OH overnight. It was then filtered, washed with 750 mL $0.1NH_4OH$ and 1L deionised water and dried in dynamic vacuum for 48 h and at 80°C for 4h. Undoped PANi dispersed on inert carrier was thus obtained.

The quantity of aniline and oxidant were reduced to 7.4 and 4.56g respectively to get a loading of 4 ± 0.5% and to3.75 and 2.32g respectively to get a PANi content 2.5 ± 0.5%. Other ingredients and conditions were similar to those described earlier.

4.3 PANi Content Evaluation

The PANi content dispersed on inert carriers was determined by determining the weight loss on heating the samples at 1700°F in an air atmosphere. The weight loss observed by heating the inert carrier alone to 1700°F was also noted and is given below

Silica -   0.2 %
Talc -   0.94%
Barium Sulfate-   0.8 %
Mica-   1.62%
Modified Mica-   1.93%

Altogether thirteen samples were prepared . The details of these samples along with their designations are given in Table I.
The conductivity of talc having 3% doped PANi was qualitatively measured.

Table I: Undoped PANI dispersed on inert carriers: Sample Designations

Serial No.	Sample Designation	Inert Carrier	% Weight Loss on Heating
1	10/19/72/S-1	talc	7.91
2	10/27/75/S-1	talc	3.73
3	11/01/76/S-1	talc	2
4	11/02/77/S-1	talc	1.15
5	10/25/74/S-1	silica	7.78
6	11/08/79/S-1	silica	3.95
7	11/08/79/S-2	silica	2.03
8	11/06/78/S-1	barium sulfate	8.08
9	11/06/78/S-2	barium sulfate	4.63
10	10/24/73/S-1	mica	7.93
11	11/15/81/S-1	modified mica	9
12	11/20/82/S-1	modified mica	5.38
13	11/20/82/S-2	modified mica	3.65

5. Coating of Corrosion Inhibitors with PANi (undoped)

Undoped PANi (Neste Corp. Finland) was dissolved in NMP. The solution was left overnight, stirred at 50°C for 3h and 95°C for 30 min. After filtration of the solution the PANi conc. was determined by evaporating a known weight of solution to dryness . A 1.2% PANi solution was thus obtained. Commercially available corrosion inhibitors Heucophos ZMP and Heucophos ZP10 were coated with PANi solution. For this purpose 10 g of inhibitor was taken and 10.2g of PANi solution was added to it. The contents were mixed thoroughly and NMP was removed slowly at 80 °C and later at 140°C. PANi coated corrosion inhibitors having 1.2% undoped PANi were thus obtained. The exact content of PANi on these inhibitors could not be determined by heating to 1700°F because of considerable weight loss observed by heating inhibitors alone.

Inert carrier Talc was also coated with 19 g of 1.2% NMP solution of undoped PANi. The PANi content as determined by heating the coated sample to 1700°F in air atmosphere was found to be 2.1%.

6. Preliminary Testing of Corrosion

Mild steel plates cleaned with acetone,wire brush and wiped with tissue paper were used.
Binder Resin: Epoxy resin (DER 331) and diethylene triamine were used.
Corrosion inhibitor: Zinc phosphate (Halox) , 10g, was mixed with DER 331 (45.3g) and 15g xylene were added. A homogeneously dispersed paste was obtained by ball milling for 2h. This paste has been designated as solution A subsequently.

(a) Solution A,10g, and DETA,0.72g, were mixed thoroughly and degassed for 10-12 min. in a vacuum dessiccator and then this solution was coated on to the cleaned SS plates using a rod.

(b) Solution A,10g, and 0.7g PANi (undoped):DETA were mixed thoroughly and coated on SS plates as described above. (The PANi:DETA complex was obtained by heating 0.5g undoped PANi with 17g DETA at 100°C for 2.5h).

(c) DER 331,10g, and 1.1g DETA were mixed well and coated on the steel plates.

The coated panels were cured at room temp. for 5 days and at 80°C for 3h.

The coated panels were scribed and placed in 0.1N HCl bath.

No difference in the performance of (a) and (b) panels was observed. Adhesion was poor and coating in (c) peeled off after 2 weeks. The panels (a) and (b) were taken out from acid bath after 2 weeks and placed in water. No difference in performance was seen under optical microscope.
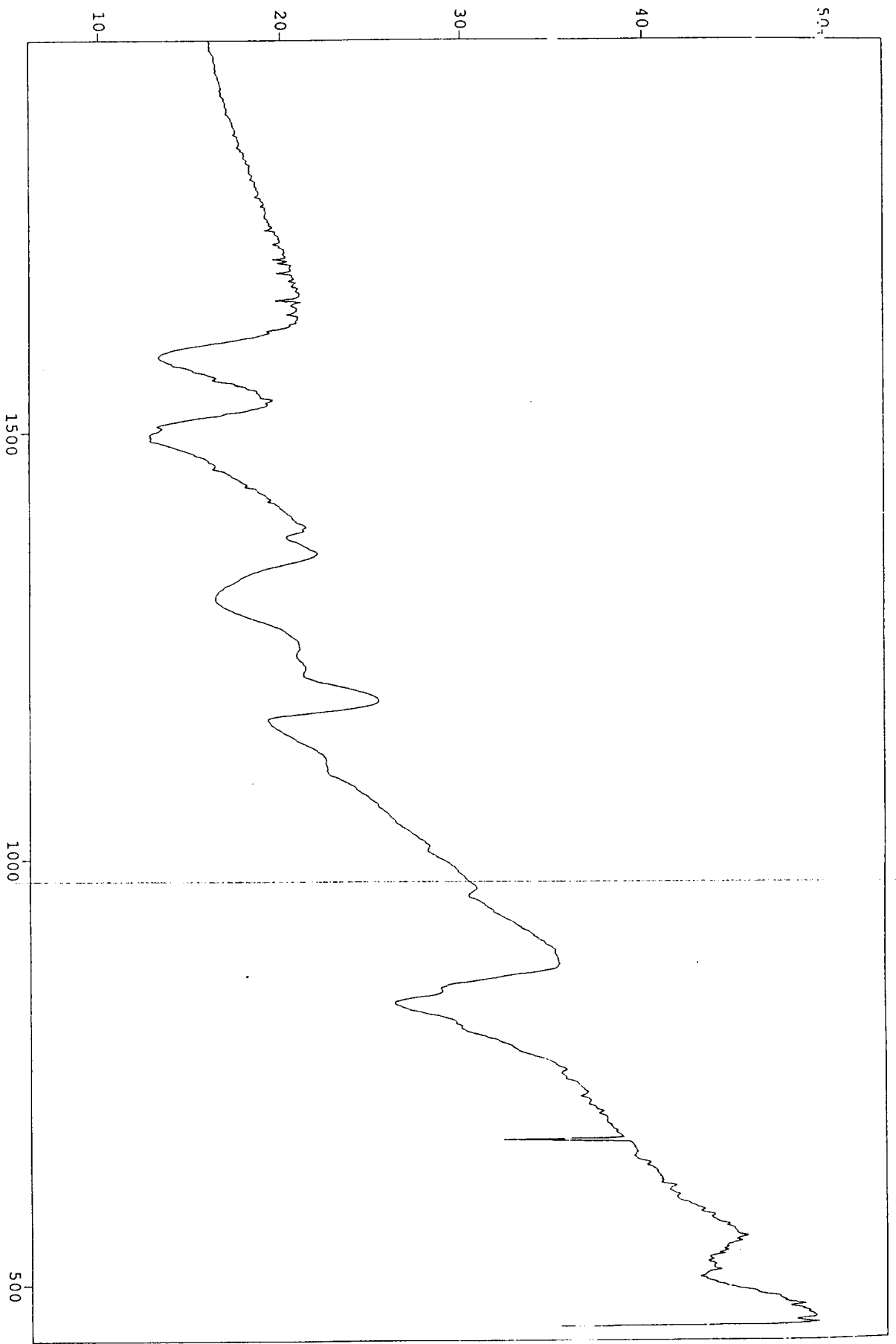
Transmittance / Wavenumber (cm-1)
File #11 : VARMA_2

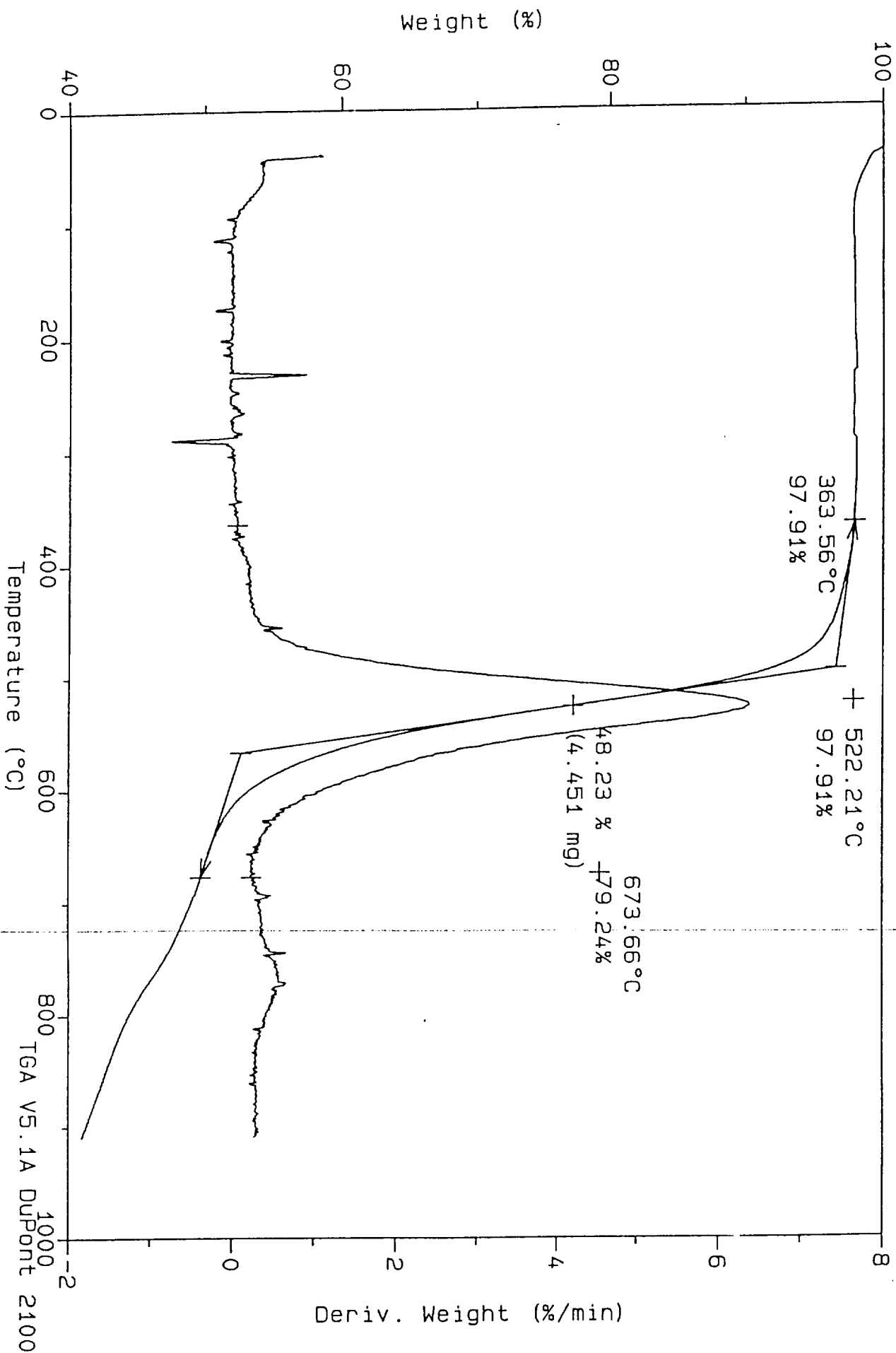FIG 1.   UNDOPED PANi

Paged Y-Zoom CURSOR
8/30/95 1:26 PM Res=2cm-1

Sample: UNDOPED PANI
Size: 9.2300 mg
Method: 10°C/MIN
Comment: 10°C/MIN, N2 PURGE

T G A

File: A:VM.003
Operator: IKVARMA
Run Date: 28-Nov-95 13:38

Weight (%)

363.56°C
97.91%

522.21°C
97.91%

48.23 %
(4.451 mg)

673.66°C
79.24%

Temperature (°C)

Deriv. Weight (%/min)

TGA V5.1A DuPont 2100

FIG. 2.

Sample: 11/2/77/S-2 DOPED
Size: 12.0100 mg
Method: 10.0 C/MIN
Comment: 10°C/MIN, N2 PURGE

TGA

File: A:VM.08
Operator: IKVARMA
Run Date: 4-Dec-95   11:55

145.57°C

7.463 %
(0.8963 mg)

239.32°C

354.70°C

297.01°C

515.76°C

34.31 %
(4.120 mg)

765.76°C

4.916 %
(0.5904 mg)

Weight (%)

Temperature (°C)

[- - -] Deriv. Weight (%/°C)

TGA V5.1A DuPont 2100
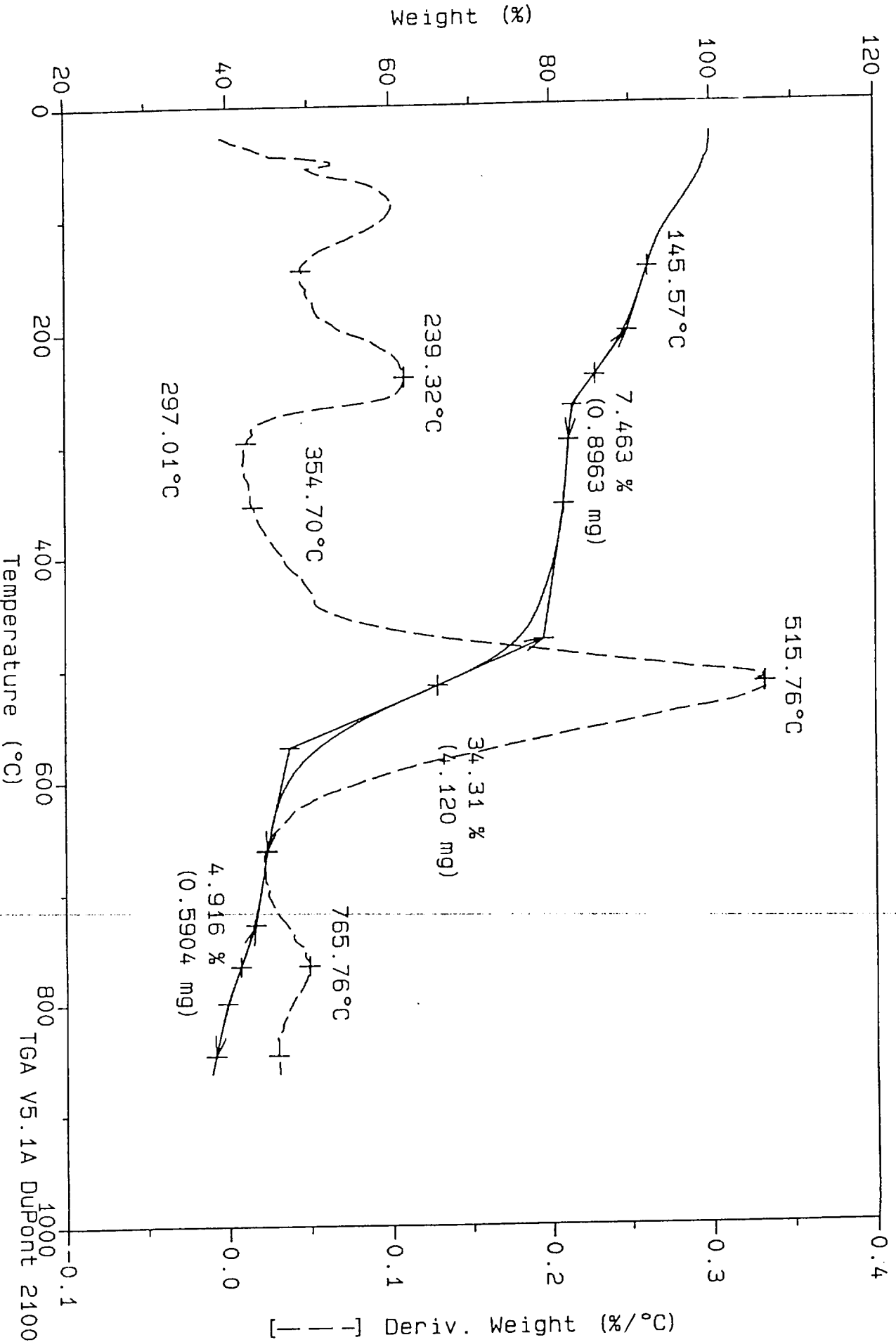
Fig. 3

Sample: PANI EPOXY
Size: 9.9300 mg
Method: 10°C/MIN

DSC

File: C:VA.02
Operator: I.K. VARMA
Run Date: 10-Aug-95 10:43

Heat Flow (W/g)

114.29°C

177.12°C
13.19J/g

245.46°C

Temperature (°C)

DSC V4.0B DuPont 2100

FIG. H

Sample: PANI EPOXY
Size: 9.9300 mg
Method: 10°C/MIN

DSC

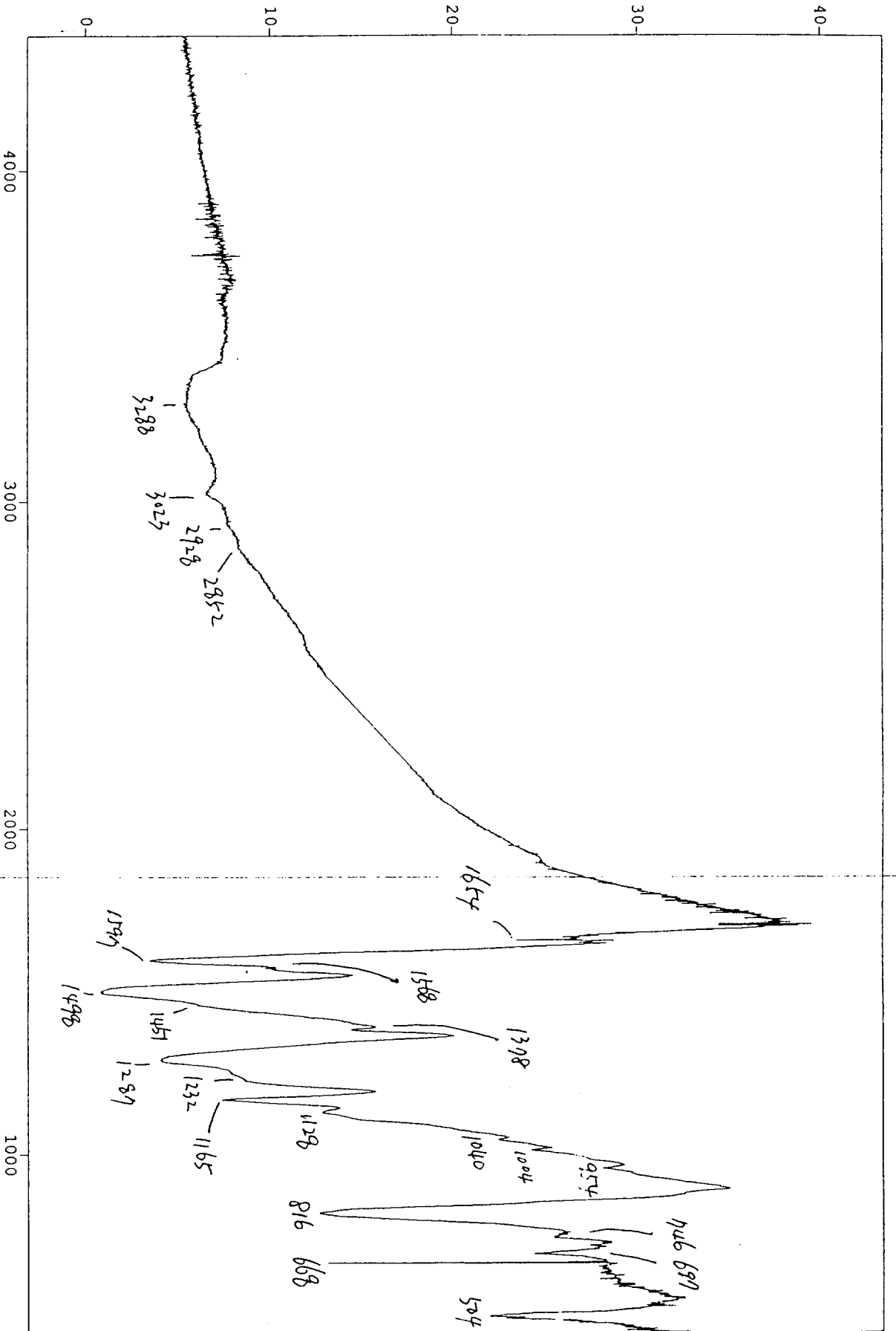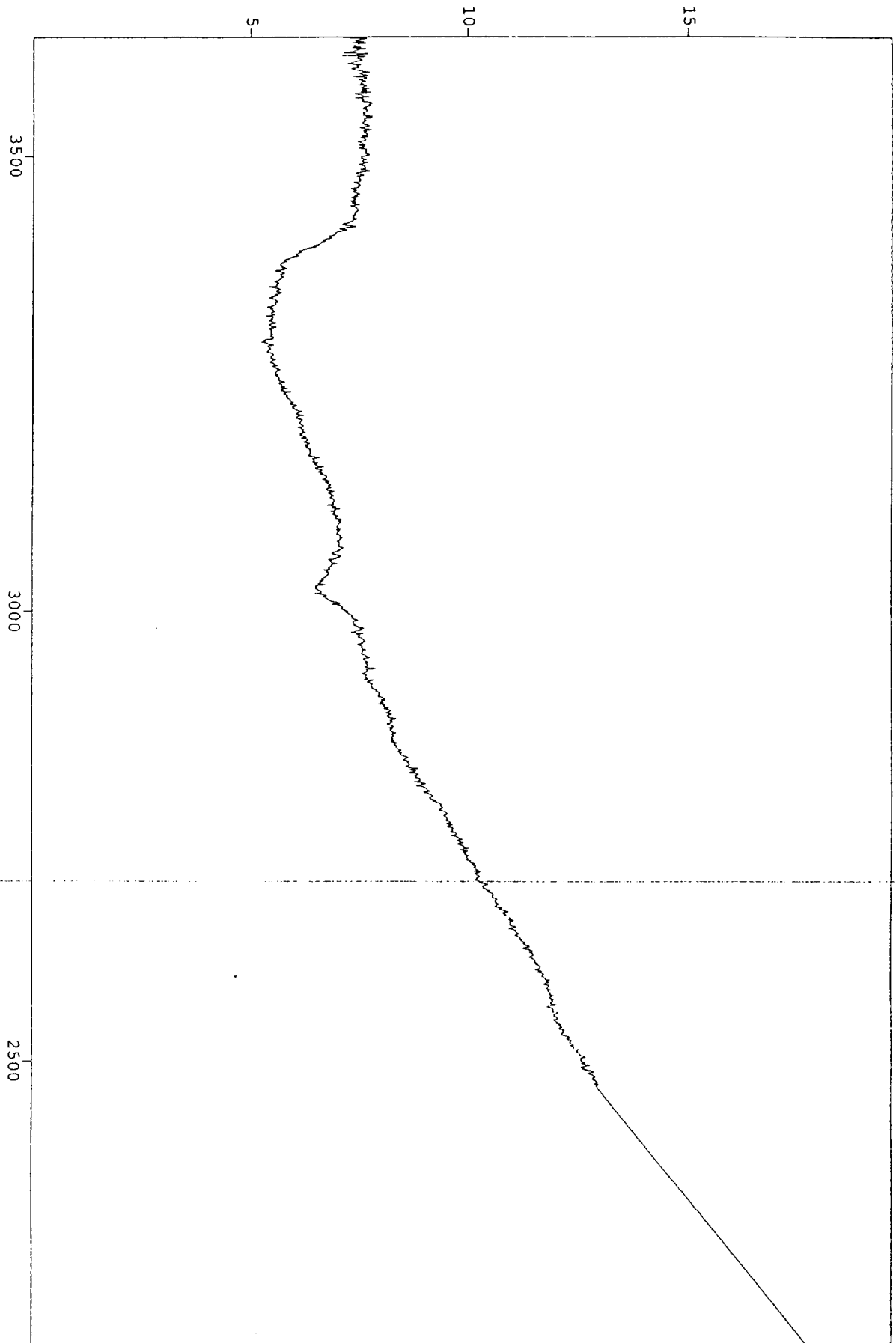File: C:VA.02
Operator: I.K.VARMA
Run Date: 10-Aug-95 10:43

Heat Flow (W/g)

Temperature (°C)

114.23°C

FIG. 4

DSC V4.0B DuPont 2100
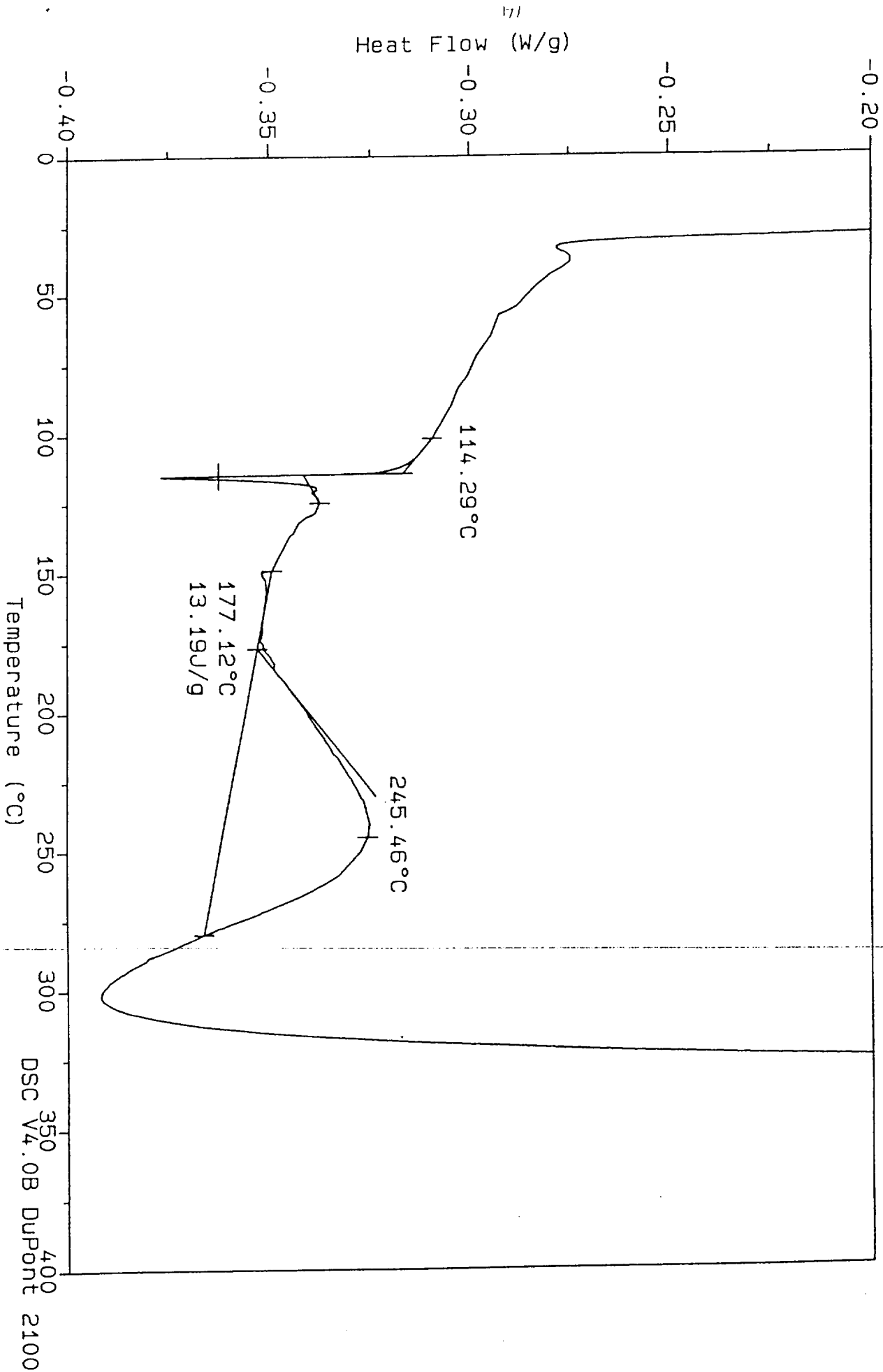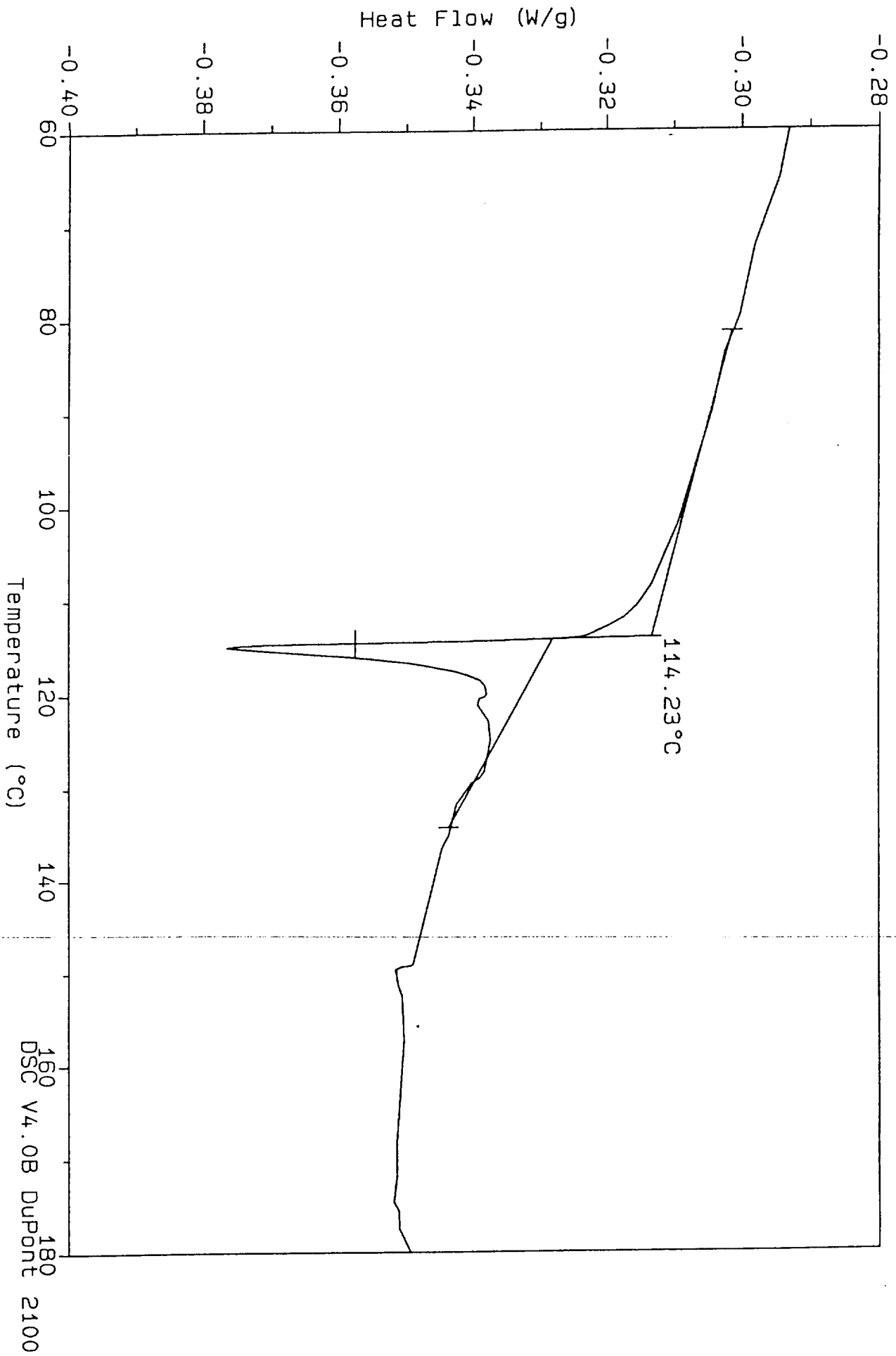
Transmittance / Wavenumber (cm-1)

File # 1 : VARMA

Fig. S   UNDOPED PANI - DETA adduct

Paged Y-Zoom CURSOR

8/29/95 10:07 AM Res=2cm-1

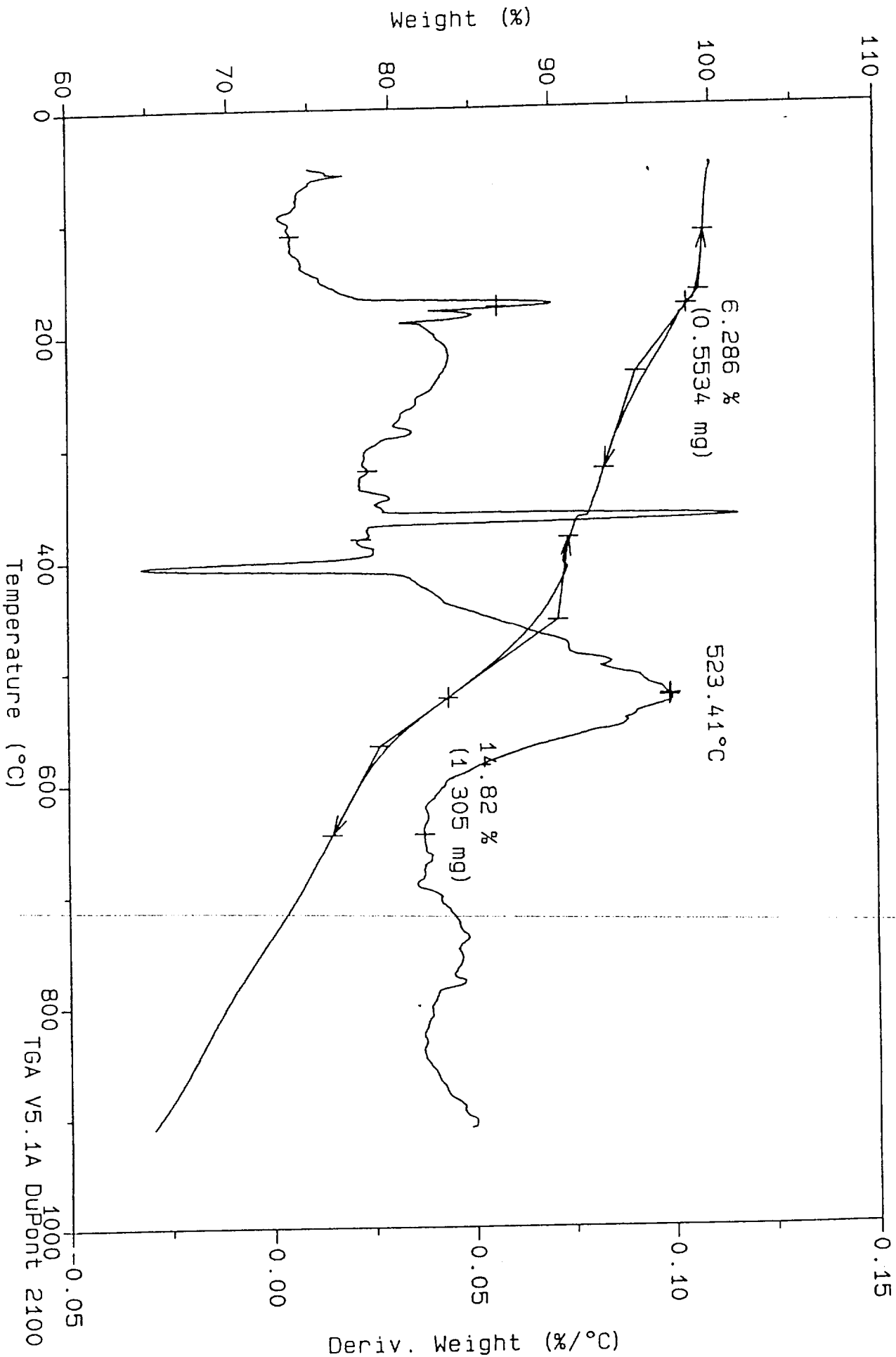Transmittance / Wavenumber (cm-1)

File # 1 : VARMA

Paged Y-Zoom CURSOR

8/29/95 10:07 AM Res=2cm-1

Fig. 5   Undoped PANi - DETA adduct

FIG 6.

Sample: POLY(M-ANILINE) UNDOPED
Size: 9.9440 mg
Method: 10.0 C/MIN
Comment: 10°C/MIN, N2 PURGE

TGA
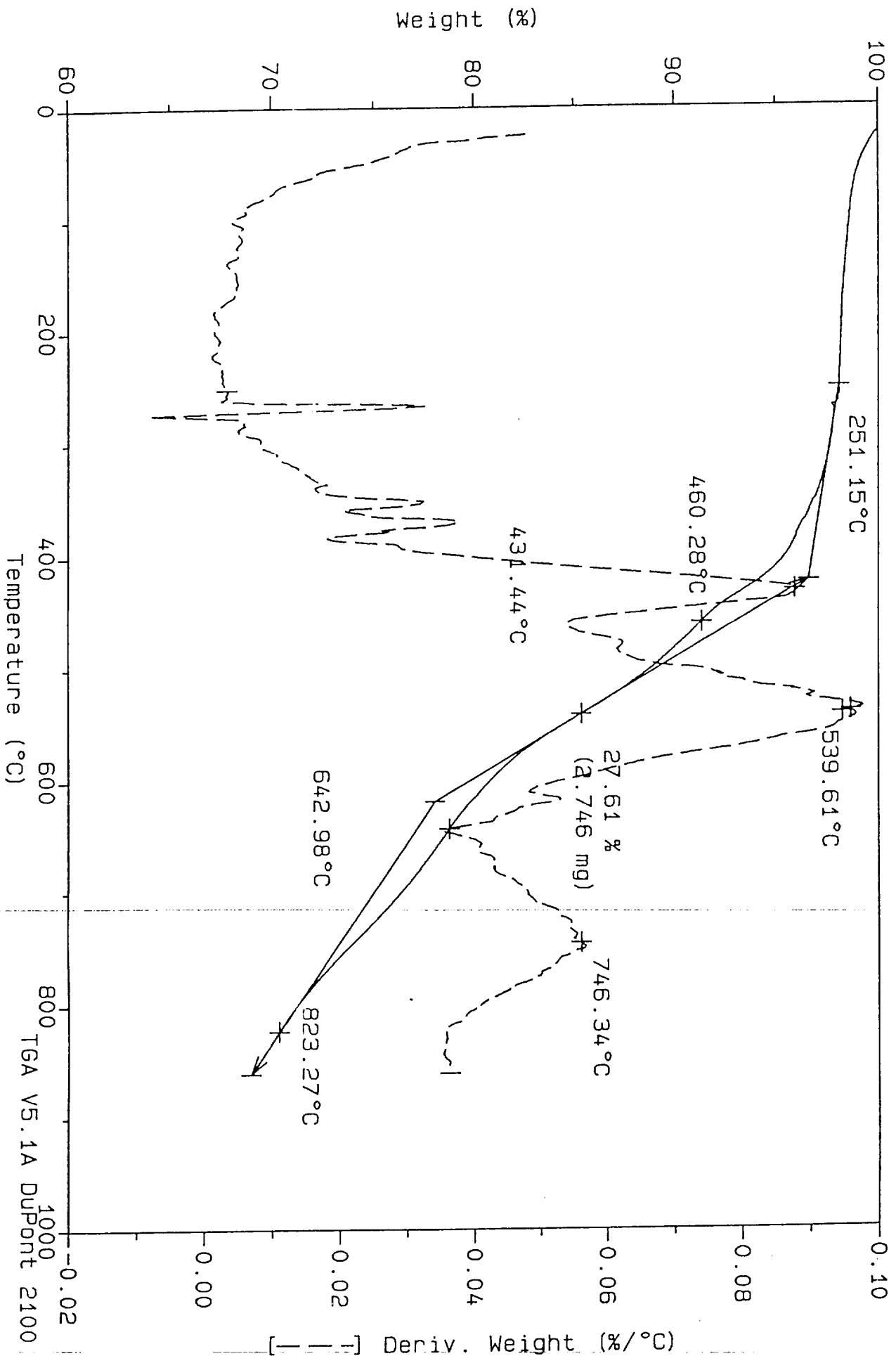
File: A:VM.10
Operator: IKVARMA
Run Date: 7-Dec-95 09:52

251.15°C

460.28°C

434.44°C

539.61°C

642.98°C

27.61 %
(2.746 mg)

746.34°C

823.27°C

Weight (%)

Temperature (°C)

Deriv. Weight (%/°C)

TGA V5.1A DuPont 2100

Fig. 7