RELIABILITY OF ELECTRONIC DEVICES CONTAINING EPOXY RESINS

Dr. J. C. Spitsbergen
EPOXY CONSULTING, INC
Franklin Lakes, NJ
RELIABILITY OF ELECTRONIC DEVICES CONTAINING EPOXY RESINS

Dr. J. C. Spitsbergen, EPOXY CONSULTING, INC

Abstract

Epoxy resins, because of their favorable balance of properties including high adhesion and strength, and resistance to heat, chemicals and moisture, along with low shrinkage and dielectric constant, have been widely used in the packaging of electronic circuits containing silicon die, typically IC’s, to achieve high reliability. Thus, conductive adhesives have generally replaced solder for die attach. When the more compact flip chip is used, the thermal cycling failure time can be extended by epoxy resin encapsulation. Further, although die coatings have been applied using many types of polymers, which may excel an epoxy resin based coating in any one property, epoxy resin based coatings should provide higher reliability due to their better property balance. In addition, except for extreme conditions (such as very high temperatures), lower cost post-molded epoxy resin based encapsulations are as reliable as hermetic packages. This is shown by many studies of field results as well as by predictions using environmental stress testing. Even lower cost as well as decreased size, while maintaining the reliability comparable to hermetic devices, appear possible through an epoxy resin based upgraded glob top process. It is shown that epoxy resin glob top encapsulations can be formulated to easily exceed 1000 hs. in 85°C/85% RH testing. Studies demonstrating the reliability of epoxy resin based surface mount placement and lead bonding adhesives are discussed. Thus lower cost, yet highly reliable, electronic devices can be manufactured through the use of formulations based on epoxy resins.

INTRODUCTION

Since their commercial introduction in 1947, epoxy resins, because of their favorable balance of properties including high adhesion, strength, and resistance to heat, chemicals and moisture along with low shrinkage and low dielectric constant, have been widely used for electrical and electronic applications. Upon the development of semiconductors, engineers quickly chose epoxy resins for packaging of electronic devices. During the rapid acceptance, some reliability problems occurred when devices were subjected to the severe stresses of certain applications. Advances in obtaining a very low level of ionic impurities (mainly halogens, for example, chlorine) and modification in both the resin and resin formulation to improve processability and water absorption have brought reliability up to the level of hermetic devices.

Epoxy resin formulations are used in many of the steps in the manufacture of electronic packages. These include conductive adhesives, flip chip encapsulation, die coatings, encapsulation and surface mount placement and lead bonding adhesives.

DISCUSSION

Die Attach Adhesives.

Conductive adhesives based on epoxy resins have generally replaced solder for die attach. In most formulations a high level of silver is used. Conductive adhesives provide easier, cleaner (including no solvent and lead), and lower temperature processing and better fatigue resistance with little loss in thermal and electrical conductivity.
Generally, conductive die attach adhesives are more reliable than solder\(^{(1)}\). In 1975, David
claimed that "over 1.5 million epoxy die-attachments have been delivered for use in military
and space applications. Not one field failure...due to epoxy resin die attach has been
reported\(^{(2)}\). This occurred even though die attach adhesives with high chlorine give poor
performance in the autoclave (pressure cooker) test. For example, an autoclave comparison
made on plastic encapsulated diodes at the 1980's levels of 20 to 400 parts per million (ppm)
extractable CI\(^{-}\) gave, after 96 hs, 0 failures out of 50 for 20 ppm and 22 failures out of 50
for 400 ppm\(^{(3)}\). Since extractable chlorine level typical of the 1970's was even higher (600
ppm)\(^{(4)}\), one might have predicted many field failures based on the above results for 20 to 400
ppm.

Such predictions do not hold, however, because various physical and chemical processes have
different activation energies. Therefore, reactions not important at field conditions may be
the ones that are being accelerated the most. Thus the autoclave test must be accelerating
the stresses and reactions not important for service conditions so that it may be less likely
to predict reliability under actual service conditions than 85\(^{\circ}\)C/85% RH. For example, the
121\(^{\circ}\)C temperature of the autoclave test is above the \(T_g\) of most die attach adhesives. This
leads to a pronounced increase in the coefficient of the thermal expansion (CTE) and decrease in
water resistance, accelerating these stress producing properties out of proportion to those of
a normal service environment.

The level of extractable chlorine in the 1990's is generally 10 ppm or less. Thus four epoxy
resin formulations with 10 ppm ionics gave only 1 failure out of 208 (1/208) when subjected to
2016 hs of 85\(^{\circ}\)C/85% RH while the probably too highly accelerating autoclave test gave 58
failures. In fact, a formulation with 100 ppm gave no failures during 85\(^{\circ}\)C/85% RH (0/36) and
autoclave (0/35)\(^{(5)}\). A study involving snap cures in which the extractable chlorine was 7 ppm
likewise showed the high reliability of epoxy resin based die attach adhesives\(^{(6)}\). However,
only the thermal cycling results were reported.

Normally high glass transition (\(T_g\)) are used. Low \(T_g\) adhesives, however, have been found
useful for large dies where stresses are very high, as long as temperature, physical forces
and moisture conditions are not too severe. These adhesives, although high in CTE, have a
modulus low enough to more than offset the high CTE under moderate conditions (roughly,
stresses are the product of CTE difference between the adhesive and the die or substrate,
the elastic modulus of the adhesive and the temperature range). An analysis of the effect of
material and geometric properties on stresses has been made\(^{(7)}\).

Flip Chip Encapsulant.

When a manufacturer wishes to use the more compact flip chip attachment, the thermal cycling
failure time can be extended by encapsulating the solder connections with an epoxy resin.
For example, Machuga\(^{(8)}\) compared the air to air thermal cycling between -50 and 125\(^{\circ}\)C
finding a mean time to failure (MTTF) of 38 and 3900 cycles for unencapsulated and
encapsulated, respectively. Similar 5 to 10 times improvement in thermal cycling has been
reported by others\(^{(9-11)}\). This is confirmed by finite element analysis which showed that
the stresses are shifted to the die and substrate\(^{(12)}\). Another finite element analysis\(^{(13)}\)
indicated a need for high modulus, high \(T_g\) epoxy resin for ceramic substrates.

However, the specific chemical properties of the encapsulant are important. O'Malley et
al.\(^{(14)}\) compared four silica filled, anhydride cured epoxy resin encapsulants, labelled
Materials 1 to 4. They found only one (Mat. 1) exceeded 1000 cycles of thermal shock (-55 and
125\(^{\circ}\)C, 5 min dwell). Although differences in adhesion appeared to be the main factor
affecting thermal shock MTTF, except for Mat. 3, which had a \(T_g\) of 120\(^{\circ}\)C (low), the range of
properties measured ($T_g$, viscosity, CTE and cure time) do not reveal the reason for the poor performance of Mat. 2 and 4. The authors also determined that thermal shock resistance increases with laminate thickness and decreases with die size.

When attaching to flexible substrates, particularly when high temperature cycling resistance is needed, a low stress encapsulant may be needed to survive 1000 cycles\(^{(15)}\). Other confirming data have been obtained\(^{(16)}\). Reliability is discussed further elsewhere\(^{(17)}\).

Non-solder Flip Chip.

There are procedures using anisotropically conductive (z-axis) paste or film in which solder bumps are not used\(^{(18)}\). There is also a procedure (polymer flip chip) in which the conductive epoxy resin bumps are screen printed onto the chip\(^{(19,20)}\). Reliability is indicated by essentially no change in resistance for 160 unencapsulated resistor networks (under-filled with a low viscosity epoxy resin to prevent contact oxidation) when subjected to 100 thermal cycles\(^{(21)}\). Reliability data on IC's is in progress. Another set of packaged resistor networks, each containing four resistors, show after thermal cycling from -45°C to 100°C, about the same average increase in resistance of about 15 mohms as for wire bonded\(^{(22)}\).

Die Coating.

Many types of polymers are used for this application. Examples are acrylic, urethane, epoxy resin, silicone, polyimide\(^{(23)}\) and polyethylene. No studies on the reliability of epoxy resin die coatings are available. Coating the die with a silicone gel has been shown to improve reliability. Tests were run on plastic encapsulated C-MOS (72 I/O). For 85°C/85% RH there were no failures after 1000 h while for thermal cycling from -55°C to +150°C there were no failures on 21 samples after 1000 cycles. However, no comparison with the absence of the silicone gel was made\(^{(24)}\). Another die coating study involving silicone gel as the encapsulant has been made recently\(^{(25)}\). This will be discussed later. With the availability of low hydrolyzable epoxy resins such coatings may not be necessary. In the case of post-molded devices passivation with silicon, aluminum and boron hydride have lead to improved reliability.

Post-molded Encapsulation.

Post-molding is the process in which a solid encapsulant in the form of a preformed molding compound pellet is applied through a transfer molding process in contrast to pre-molding in which the device is placed in a molded case and sealed. For large volumes, post-molding is the most economical method of encapsulation.

Constant improvement in molding compounds along with more effective use of die coatings (to reduce stresses during thermal cycling)\(^{(23)}\) and die passivation with nitrides (to reduce corrosion from moisture) (as well as improved package design and quality procedures) have lead to high reliability. This is shown by several compilations of data. Data collected by Frank\(^{(26,27)}\) on commercial plastic encapsulated devices show failure rate decreased from about $5 \times 10^{-6}$ in 1978 to $0.5 \times 10^{-6}$ failures/h in 1986 while data obtained by Watson et al.\(^{(28)}\) show a decrease from $100 \times 10^{-6}$ in about 1978 to $0.05 \times 10^{-6}$ failures/h in 1990. Current failure rates for specific IC packages have also been reported\(^{(29)}\). Further, it has been reported that generally the cumulative failure rate for temperature humidity bias testing (THB) (for example, 85°C/85% RH for 1000 h) has decreased from 25% in 1974 to 0.1% in 1990\(^{(30)}\) and specifically for DRAMS from about 50% in 1980 to about 0.01 in 1990\(^{(31)}\). These improvements have provided reliability equivalent or higher than hermetically sealed.
packages for most applications, particularly when environmental conditions are somewhat constant or not extremely severe. Consequently, early failures on commercial devices in ground based applications decreased from 0.3 x 10^-5 in 1978 to 0.03 x 10^-5 failures/h in 1988 which was similar to the 1988 failure rate for ceramic devices(32).

Environmental stress test comparisons have also demonstrated the general reliability equivalency of plastic encapsulated to hermetic devices. This was demonstrated by a recently reported study comparing plastic (epoxy resin) and hermetic for protecting the same IC(33). It showed no failures after 1000 temperature cycles and 1000 hs of temperature-humidity-bias. When these same plastic (encapsulated) and hermetic IC's were placed on circuit cards and subjected to power cycling under humidity and thermal cycling no device failure occurred either. These results confirmed previous demonstrated comparability of thermal cycling reliability for plastic versus hermetic devices in terms of % failures/1000 cycles as 0.034 vs. 0.17(34), 0.44 vs. 0.36(35) and 0.083 vs. 0.07(36).

Such results confirm experience in tropical areas where hermetic devices often are less reliable than plastic encapsulated devices as reported by Sinnadurai[37]. Although such poor performance of hermetics has been reported and often ascribed to moisture penetration, the actual amount of humidity environmental testing of hermetics has been very limited because of the belief that they were impenetrable to moisture. Thus even Sinnadurai[38] in a comparison that showed the greater reliability of plastic encapsulated over hermetically sealed IC op-amps; conducted only 150°C high temperature environment. The plastic encapsulated devices had a cumulative failure of about 10% while for the hermetic it was about 40% (perhaps at high temperature any residual moisture is driven away from the IC whereas it is trapped in the hermetic device). It must be assumed then that the higher rate of tropical failure reported was due to temperature rather than humidity (although some failures were due to poor seal). This should be applicable to hybrid devices and multichip modules (MCM), thus providing lower cost products.

Much commercial data[39] and experimental literature(41,42) show transfer molded plastic encapsulated devices can exceed 1000 to 2000 hs. in an autoclave at 121°C, 1000-2000 cycles of thermal cycling from -65 to 150°C and 1000 hs. at 85°C/85% RH without failure. In addition, an expectation of exceeding 1000 hs at highly accelerated stress testing (HAST), generally 140 to 150°C, 90% RH, may be developing even though HAST may be even less predictive of reliability under service conditions than the autoclave test. Further, the reliability of epoxy resin molding compounds is constantly being improved(43,44).

The above-mentioned environmental stress tests certainly are not reliable for predicting reliability unless the physics-of-failure (as well as chemistry), which considers first principles with regard to stresses rather than assuming steady state conditions and constant Arrhenius kinetics, are taken into account(42). Considerations such as temperature and humidity conditions at steady state, gradients, rate and range of variation as well as how systematically variations occur are involved. Because of the high reliability of post-molded devices the testing time to achieve failure for an 85°C/85% RH test becomes impractical. As a result much testing is done under autoclave and even HAST conditions, thereby making the THB test even less useful for extrapolation to service conditions.

With the prominence of surface mount devices a preconditioning environmental 85°C/85% RH test has been important to properly determine reliability due to the tendency for the molding compound to absorb moisture which then expands to form steam at reflow temperatures. Although audible pops and obvious cracks are easily detected, such expansion can cause delamination and possibly cracks which may not be detected. The preconditioning procedure may be as elaborate as first temperature cycling from -65 to 150°C, then 10 cycles of dry
bake at 125°C followed by 85°C/85% RH for 48 hs and then solder reflowing three times at about 260°C(41). The problem has been particularly troublesome for thin packages. The use of highly filled biphenyl epoxy resin has lead to considerable improvement(41), although flowability and high temperature strength is lessened. The preconditioning is being replaced by the manufacturer labeling components according to the six level IPC-SM-786A/JEDEC A112 Moisture Level standard(45).

Popcorn cracking in the epoxy resin encapsulant also can be a problem for ball grid array (BGA) (important for high I/O and large die sizes). With regard to THB, BGA devices were able in 1993 to pass 85°C/30% RH and 30°C/60% RH by restricting the time at ambient conditions(46); with regard to thermal cycling, the limitation appears to be in the solder ball(47).

The high reliability of plastic encapsulation can be useful for MCM-L, which is basically a PQFP device in which a tiny PCB containing several dies is encapsulated instead of one die on a lead frame(48).

Liquid Encapsulation of IC’s.

Another approach to lower cost through plastics while maintaining reliability is to upgrade the chip on board (COB) or glob top process. Recent studies using a 7.6 by 19.1 mm (0.3 by 0.75 in) dice encapsulated with state-of-the-art epoxy resin glob top show it passing 2500 thermal cycles, 1500 thermal shocks, 1100 hs. of autoclaving, and 1400 hs at 150°C can be passed(49,50). Two experimental formulations shown in the same studies may even give more reliability. Other recent data show an epoxy resin based glob top passing 1000 hs of 85°C/85% RH and 1000 hs of high temperature operation at 125°C(51). No information, however, is given on formulation or test location. Applications for glob top include MCM’s, particularly MCM-L(52). Further, the reliability of epoxy resin glob tops is constantly being improved(53,54).

Other polymers have been proposed for glob top. So far, however, sufficient data have been obtained to conclusively demonstrate high reliability only for epoxy resin based glob tops. In fact, not too long ago a Reliability without Hermiticity (RwoH) group was emphasizing the use of silicone, rather than epoxy resin as the ultimate for reliability(55,56). RwoH studies have shown better HAST reliability for silicone glob tops. However, glob tops being used commercially are based on epoxy resin because of epoxy resin’s better balance of properties, including having higher mechanical strength, higher adhesion, lower CTE and greater resistance to contaminated water(25-27) (although epoxy resin compounds absorb more water, their much lower permeability to water than silicone leads to lesser migration to the metallization of the ions that lead to corrosion).

Actually, the at that time "state-of-the-art" epoxy resin glob tops, which had a much higher hydrolyzable chlorine than current formulations, did not fail 85°C/85% RH after 2500 hs with bias (amount of volts not disclosed)(58). As the technology improved, even higher reliability was indicated by environmental stress testing by 85°C/85% RH and thermal cycling(59,60,61,62).

HAST conditions assume the Arrhenius relationship between temperature and reaction rate is the same so that all reactions involved are accelerated equally. Such is not usually the case. For example, the breakdown of the covalent bromine-carbon bond to release bromine from the flame retardant resin component of the molding compound does not become important until temperatures much higher than 85°C are reached. Thus at the elevated HAST condition considerable bromine, as well as chlorine, from the breakdown of the covalent chlorine-carbon
bond are present which would essentially remain tied up at lower temperature. Further, the HAST test temperature is considerably above the \( T_g \) of most epoxy resin formulations so that not only is the CTE much higher than most service conditions but also the formation of condensed water in probably prevented. Such elevated tests are not very predictive since physics of failure principles are ignored. For example, what does testing at a constant high temperature and humidity predict when devices may be subjected to a climate where long periods of high humidity and temperature are followed by a drastic drop in temperature causing condensation of water within the device \(^63\). Pecht et al. \(^64\) discuss many other effects, including those which affect reliability of electronic devices adversely as the temperature decreases.

**Lead Bonding.**

This takes the form of both screen printable paste and film. Application is mainly for surface mount. Typical properties for pastes are shown in Table I \(^65\).

Eventually the conductive epoxy resin adhesive will replace solder because of the advantages of lower temperature bonding, resiliency, no need for flux and use of lead, as well as often providing a means to simplify the process. Current acceptance has been hindered by the greater difficulty to repair, lesser adhesion to tinned copper and higher and not too stable resistance, particularly for copper junctions \(^66\). A decrease in junction resistance has been reported in the same study after 1000 hs of \(85^\circ C/85\% \text{ RH} \) for silver and gold surfaces. There may be an informal standard that the junction resistance increase should not exceed 20% after 1000 hs of \(85^\circ C/85\% \text{ RH} \) testing \(^66\). One supplier \(^67\) reports no change in junction resistance after 1000 hs \(85^\circ C/85\% \text{ RH} \) for a Sn/Pb finish. A comparison \(^65\) of adhesives and solder is shown in Table II.

Other studies confirm the reliability. For example, the joint resistance of bonded (82% silver filled epoxy resin) surface mount resistors increased from 65 to 163 mohms after thermal shock followed by 1300 thermal cycles (however, a maximum occurred after 290 cycles during the test) and to 561 mohms from 45 mohms when subjected to 1300 hs of \(85^\circ C/81\% \text{ RH} \) \(^68\). Studies using screen printed isotropic epoxy resin paste on thick-film metallizations by Nguyen et al. \(^69\) show increases in contact resistance around 1% after 1000 thermal cycles from \(-40 \) to \(125^\circ C \) and increases of 0.5 to 3% after 1000 hs at \(85^\circ C/85\% \text{ RH} \). The same study showed adhesion retention as good or better than solder after thermal cycling for 1000 cycles from \(-65 \) to \(150^\circ C \) and adequate adhesion after 1000 hs at \(85^\circ C/85\% \text{ RH} \). In another case the contact resistance increase was approximately 2% after 1000 hs of \(85^\circ C/85\% \text{ RH} \) for a snap cure formulation on Sn/Pb solder \(^70\). The reliability of six circuits with anisotropically conductive paste adhesives for one formulation \(^65\) showed an average resistance of 66 mohms after 1000 hs of \(85^\circ C/85\% \text{ RH} \) and an average resistance of 48 mohms after 1000 cycles of \(-40 \) to \(+150^\circ C \). In another example of anisotropically conductive paste adhesives, it was found that for a paste having a \( T_g \) of \(-25^\circ C \), the DC resistance was stable at approximately 2 mohms after 500 thermal stress cycles of \(-40 \) to \(93.3^\circ C \) \(^71\) while a paste with a \( T_g \) of \(84^\circ C \) increased only to approximately 3 mohms. An isotropic conductive adhesive for connecting flex circuits using polymer thick film has been reported to be highly reliable \(^72,73\).

Anisotropically conductive adhesives may be necessary for very fine pitch. Thus Liu et al. \(^74\), used anisotropic adhesives for the finer pitch PQFP’s and isotropic for large pitch in their studies. Their silver filled anisotropic adhesive formulation gave essentially no change in resistance after aging at both 70 and \(120^\circ C \) for 1096 hs when used to bond PQFP’s to a test PCB. However, only one test board out of 12 reached 600 cycles without a large increase in resistance when cycled from \(-55 \) to \(125^\circ C \). The poor results may have been due to thermal cycling above the glass transition temperature. When a gold filled adhesive used to bond a
PQFP to a PCB was cycled from -40 to 85°C there was no change in resistance after 900 cycles. However, in the case of CQPF’s all failed (probably due to formation of intermetallics from high soldering temperature). In the case of isotropic adhesives, one formulation (of 6) was outstanding showing essentially no increase in resistance for PQPF’s bonded to both pre-tinned and solder passivated PCB when cycled from -55 to 125°C (even though its glass transitions was only 80°C). The use of anisotropically conductive films has also been investigated for bonding a polyester circuit to an FR-4 PCB. After 100 hs of 85°C/85% RH an encouraging 27 out of 30 were essentially unchanged.

CONCLUSION

Epoxy resin formulations provide a means to obtain highly reliable electronic devices. Silicon dies in post-molded packages are generally as reliable as hermetically sealed packages.

REFERENCES

17. D. D. Chang et al., "Design considerations for the implementation of anisotropic conductive adhesive interconnection", Nepcon West Proc. 42 (1992) 1381-9; see also Ref. 18.
41. P. Jain, "296 lead fine pitch (0.4 mm) thin plastic QFP package with TAB interconnect", 44th Electronic Comp. Tech. Conf. (1994) 50-5.
58. T. Onishi et al., "Chip on board branches out: High reliability for VLSI devices has been demonstrated", Electronic Technology Int'l., Cornhill Publications (1991); see also Refs. 54, 65.
67. Alphametals, "Poly-Solder\textsuperscript{TM}, one part electrically conductive adhesive paste", Preliminary Data Sheet, Rev. 1.1, undated. See also Ref. 66.
Table I. Typical Properties of Snap Cure Screen Printable Conductive Adhesives\(^{(65)}\).

<table>
<thead>
<tr>
<th>Property</th>
<th>Isotropic</th>
<th>Anisotropic</th>
</tr>
</thead>
<tbody>
<tr>
<td>T(_o), (^{\circ})C</td>
<td>120</td>
<td>123</td>
</tr>
<tr>
<td>Vol. resistivity, ohm-cm</td>
<td>0.00033</td>
<td>0.0001 (parallel)</td>
</tr>
<tr>
<td>Thermal conductivity, W/m(^{\circ})C</td>
<td>7.2</td>
<td>-</td>
</tr>
<tr>
<td>TCE, (^{\circ})C \times 10(^{6})</td>
<td>-</td>
<td>67</td>
</tr>
</tbody>
</table>

Table II. Comparison of Conductive Adhesives and Solder\(^{(65)}\).

<table>
<thead>
<tr>
<th>Property</th>
<th>Isotropic adhesive</th>
<th>Anisotropic adhesive</th>
<th>Solder</th>
</tr>
</thead>
<tbody>
<tr>
<td>Screen print</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
</tr>
<tr>
<td>Dispensable</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
</tr>
<tr>
<td>Cure temperature, (^{\circ})C</td>
<td>175</td>
<td>175</td>
<td>200 to 230</td>
</tr>
<tr>
<td>Repair temperature, (^{\circ})C</td>
<td>230</td>
<td>230</td>
<td>260</td>
</tr>
<tr>
<td>Flux removal</td>
<td>N</td>
<td>N</td>
<td>Y</td>
</tr>
<tr>
<td>Specific gravity</td>
<td>1.1</td>
<td>3.2</td>
<td>8</td>
</tr>
<tr>
<td>Thickness, microns</td>
<td>20</td>
<td>30 to 40</td>
<td>150 to 200</td>
</tr>
<tr>
<td>Cure pressure, MPa (psi)</td>
<td>0</td>
<td>0.04 to 0.2 (5.7 to 28)</td>
<td>0</td>
</tr>
</tbody>
</table>
BIOGRAPHY

James C. Spitsbergen, PhD

Dr. Spitsbergen is the consultant for EPOXY CONSULTING, INC., Franklin Lakes, NJ. He provides solutions to formulating, processing, testing and reliability problems of epoxy resin and other thermoset formulations used in electrical and electronic components and other applications. He is a member of the Board of Directors of the Electrical and Electronic Division of SPE where he served as the RETEC Technical Program Chairman. Industrial employment includes Unitrode Corporation, Watertown, MA (1983-5), as an internal consultant for polymers, Witco Chemical (1968-83), as a Project Leader for Polymers, and Dupont (1962-68), as a Senior Polymer Chemist. He is the author of 13 publications, the holder of four patents and a member of SPE, ACS, ISHM, IEPS, SMTA, SAMPE and IEEE. He received a PhD in Physical Polymer Chemistry from the U. of Delaware in 1962. Author can be reached at 201/848-1444.