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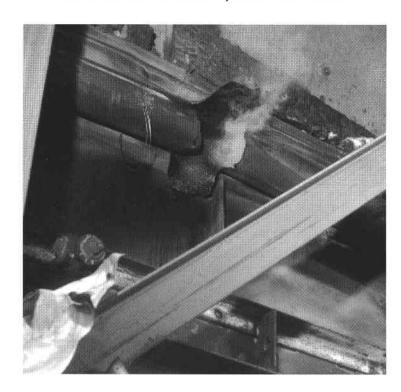


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Boiler Feedwater Pipe Failure by Flow-assisted Chelant Corrosion¹

By Crispin Hales a, Kelly J. Stevens b, Phillip L. Daniel c, Mehrooz Zamanzadeh d, Albert D. Owens e



Six-inch boiler feedwater pipe rupture

¹Reprinted from Engineering Failure Analysis 9, Crispin Hales, Kelly J. Stevens, Phillip L. Daniel, Mehrooz Zamanzadeh and Albert D. Owens, "Boiler Feedwater Pipe Failure by Flow -assisted Chelant Corrosion" pp 235-243, 2002 with permission from Elsevier Science,

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Engineering Failure Analysis

Boiler feedwater pipe failure by flow-assisted chelant corrosion

Crispin Hales ^{a,*}, Kelley J. Stevens ^b, Phillip L. Daniel ^c, Mehrooz Zamanzadeh ^d, Albert D. Owens ^e

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Abstract

On 22 April 1996, there was a catastrophic failure in a section of six-inch diameter feedwater line leading from the economizer to the steam drum on a boiler at a private industrial power plant in the Midwest. The rupture occurred immediately downstream from a chelant injection quill. Boiler water depressurized from over 900 psi and flashed to steam as it exited the ruptured pipe. A full investigation into the cause of the failure was carried out over a period of 2 years, involving experts in mechanical design, metallurgy, water chemistry and fluid flow dynamics. The boiler operating history, including water treatment methods, was carefully reviewed. Inspections were also carried out on the equivalent feedwater piping and injection quills removed from five other boilers operating with the same source of feedwater but with independently controlled rates of chelant injection. The failure occurred due to progressive thinning of the pipe wall from the water side to the point where it could no longer tolerate the operating pressures and temperature. It was concluded that thinning of the carbon steel pipe wall had been caused by a specific mechanism, termed here "flow-assisted chelant corrosion". The difference between this and flow-accelerated corrosion (FAC) is presented and recommendations are offered to help avoid similar failures in the future. Other potential causes of the failure including direct erosion and non-flow assisted corrosion were evaluated and shown to be non-causal, © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Boiler failures; Corrosion; Rupture

1. Description of the boiler

The boiler on which the failure occurred is a coal-fired unit of 275,000 lb/h steaming capacity, manufactured by The Babcock & Wilcox Company in 1962. After about 5 years of operation a larger air heater

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was installed and the all-welded Schedule 80, 6-inch feedwater line from the economizer to the steam drum was re-routed and replaced to accommodate the change. In about 1977 an injection quill was installed in this section of pipe for chemical dosing of the feedwater. The basic geometry of the pipework from the outlet of the economizer to the steam drum is shown diagrammatically in Fig. 1. The feedwater flows out of the economizer directly into a pipe tee which turns the flow vertically upwards through a long-radius bend. Inserted into this curving pipe, at right-angles to the flow, was a thermocouple well tube fitting, used for temperature measurement. The flow then passes through a horizontal 90° long-radius butt-welded elbow, and into a 15 ft straight section of pipe. The quill was installed in a horizontal plane into the flow at the upstream end of this section of the feedwater line, purposely to avoid any potential corrosion problems at the long-radius butt-welded elbow downstream. The final section of the feedwater line is an 8.5 ft vertical riser, ending with a further long-radius elbow connected to the steam drum. Within the steam drum is a distributor pipe to ensure even flow and good mixing of the feedwater as it enters the steam drum.

The boiler is reported to have been operating normally at the time of the failure, and its original performance has been maintained by feedwater treatment according to consultant service agreements. While the boiler typically utilizes Eastern coal as a fuel source, other fuels including tires, in-plant generated RDF, and Western coal have been utilized in small percentages. The unit has generally been operated in the upper range of capacity (i.e. above 200,000 lb/h) in order to meet plant demand. The main plant steam header is maintained at 850 psig and 900°F, while feedwater is controlled to approximately 925 psig and 400–414°F as it exits the economizer. Annual inspections concentrated on boiler pressure parts within the boiler itself, between the feedwater inlet valve and steam outlet stop/check valve. Note that only recently have companies begun to perform periodic detailed inspections on feedwater piping systems external to the boiler proper, although in nuclear facilities such inspections have been included for several years. A summary of the boiler history prior to the feedwater line rupture is provided in Fig. 2.

2. Rupture of the feedwater line

Shortly after the catastrophic failure in the section of feedwater line shown in Fig. 1, it was concluded that the pipe rupture was caused by internal wastage of the pipe wall. Measurements showed that prior to

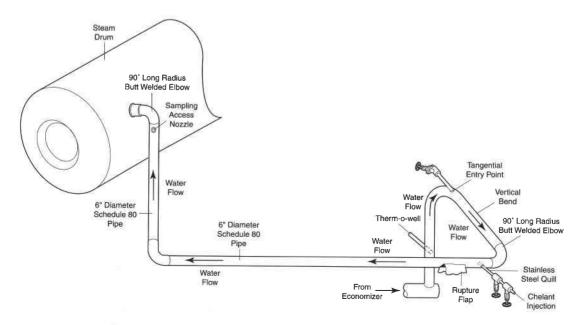


Fig. 1. Schematic of feedwater line from economizer to steam drum.

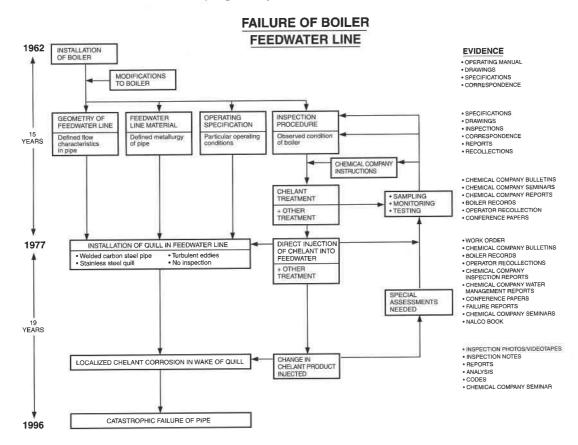


Fig. 2. Summary of boiler history prior to feedwater line rupture.

actual failure, the pipe wall thickness in the area of the rupture flaps was about 0.050 inches, which corresponds to a hoop stress in excess of the tensile strength of the SA 106 Grade B carbon steel material at the normal operating pressure.

Early in the investigation several wastage mechanisms were suggested. These included cavitation damage, flow-assisted corrosion, and chelant corrosion. The complete section of pipework between the economizer and the steam drum was removed and stored in sections. The 8-ft long section shown in Fig. 3 was carefully sawn out and preserved with dessicant. This included the upstream elbow, the quill, the rupture and a downstream length. A series of specific samples were machined out of this section for visual measurement and metallographic analysis, as well as to provide viewing ports into the pipe for inspection purposes.

3. Potential failure mechanisms

3.1. Cavitation damage

Abrupt flow discontinuities can cause low-pressure transients, and such transients can pull flowing liquid apart to form empty or vapor filled cavities. Where pressure increases just beyond the flow disruption, the cavities collapse and the implosion can damage adjacent surfaces [1]. Shock waves from collapse of the cavities deform and cold work the surface layer of steel until material is lost from the surface. The result is a very rough surface with a ragged grit-blasted or mossy appearance [2]. Consequently, surfaces of cavitation pits in steel are much rougher than those of corrosion pits. The surface does not have the scalloped



Fig. 3. Six-inch boiler feedwater pipe rupture.

appearance of flow-assisted corrosion, nor does cavitation produce the smooth well-formed pits with crisp edges characteristic of electrochemical (e.g. oxygen or acid) pitting. An objective measure of cavitation damage is the depth of metallurgical deformation, distortion of metal grain structure, and work hardening.

Cavitation damage ranges from purely physical damage to cavitation-accelerated corrosion. The relative contributions of the two processes depend on the physical severity of cavity collapse, corrosiveness of the liquid, metallurgical toughness of the metal, and corrosion resistance of the metal. Cavity collapse disrupts the liquid boundary along the steel surface and causes turbulence in the liquid. In corrosive liquids, these effects promote dissolution of the surface oxide that normally impedes corrosion. A combination of physical wastage and corrosion mechanisms accelerates the growth of surface fatigue cracks and leaves an especially ragged-mossy appearance. Where the corrosiveness of the liquid completely dominates over the removal of metal by physical deformation, the appearance of the steel surface may well be that of flow-assisted corrosion, which is then identified as the dominant wastage mechanism.

Cavitation is the result of implosion of vapor bubbles some tenths of a millimeter in diameter within the boundary layer between liquid and solid surfaces. The extent of damage to the surface depends on plastic deformation and the associated work hardening which occurs.

There are two forms of stressing to which the material is subjected:

- 1. The mechanical effect.
- 2. Fatigue, resulting from the rapid succession of impacts.

Soft metals subjected to cavitation conditions immediately begin to show signs of plastic deformation (slip lines, extrusions and intrusions form) on the surface. In the case of hard metals the cavitation process leads to fatigue cracks. Distinguishing characteristics of cavitation attack are:

- Intensive plastic deformation
- Slip lines
- Fatigue cracks
- Craters of various sizes
- Folded material from the rims of the craters

- Indication of grain boundary separation
- Fragments and fractured particles of various sizes

A metallurgical evaluation of the failed area exhibited in Fig. 4 did not show any signs of plastic deformation or the associated work hardening. There was no evidence of fatigue cracks, slip lines, extrusions or intrusions, nor any of the aformentioned features indicative of cavitation damage in the samples taken from the immediate location of the failed area.

3.2. Flow-accelerated corrosion (FAC)

Flow-accelerated corrosion (FAC) is the chemical dissolution of surface oxide and metal, accelerated by flow and flow impingement [3,4]. There are no physical or microstructural changes in the steel, making flow-accelerated corrosion easy to distinguish from cavitation damage.

The solubility of iron and iron oxide in water depends on the pH, temperature, oxidizing potential, and the concentration of chemical agents (such as chelants) that form soluble iron complexes. To prevent corrosion of piping, boiler feedwater is treated to reduce its ability to dissolve and corrode steel. For example, it is deaerated and chemicals are added to increase its pH. FAC can occur in both single phase (liquid), and two phase (steam and water) systems. Piping containing even small traces of molybdenum, copper, and particularly chromium has been shown to resist FAC. "Chrome-moly" pipe such as P11 and P22, as well as stainless steel pipe, show substantial resistance to FAC.

High flow rates, turbulence, and especially flow impingement increase water-steel contact and thereby increase the rate of iron dissolution and corrosion. Flow-accelerated corrosion is most severe at abrupt flow discontinuities in the intermediate temperature area of piping where iron oxide solubility is highest. To the extent that treated feedwater remains corrosive, corrosion rates are higher on the outside of pipe bends and tees and at turbulence promoters such as irregular welds or changes in pipe diameter. In areas of flow-accelerated corrosion, the interaction of flow and the electrochemical processes of corrosion produce a characteristic wastage pattern. The surface appearance ranges from smooth to pitted, but a distinctive

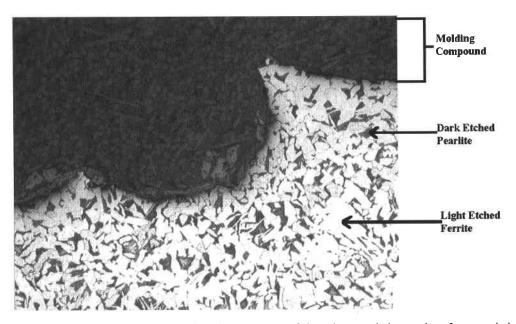


Fig. 4. Photograph at $100 \times$ magnification exhibiting the microstructure of the tube sample internal surface consisting of dark etching pearlite in a matrix of white etching ferrite. Etched in 2% nital. The sample was taken from the failed area of the pipe. No evidence of plastic deformation was observed in this area.

wave-like appearance with smooth scallops and sharp crests is generally prevalent in the areas of more severe wastage.

3.3. Chelant corrosion

Chelants, generally EDTA (ethylenediaminetetraacetic acid) and NTA (nitrilotriacetic acid), are organic chemicals that react with hardness minerals to form soluble chemical complexes and, therefore, can be used to keep boiler water minerals in solution [5]. They have been used successfully for decades in numerous industrial boilers. With appropriate application and control, they are effective and reasonably safe. However, as with other treatment chemicals, misapplication and loss of control can cause corrosion.

Chelants have a much stronger affinity for calcium and magnesium ions, but in boiler water they also complex with iron. Iron is always at least slightly soluble in water, and chelants increase this solubility. This effect is more pronounced at higher temperatures. It can be substantial if chelant concentrations are excessive, the solution pH is low, or the solution contains excess oxygen or another oxidant. Many boiler component failures have been attributed to chelant corrosion, where one or more of these conditions have not been adequately controlled [6].

Most documented cases of chelant corrosion are within the boiler circuitry itself, where temperatures and chelant concentrations are generally higher (depending on the thermal decomposition rate). However, chelant corrosion also occurs in feedwater systems. Chelant corrosion often occurs as flow-accelerated corrosion in areas of flow impingement. The *NALCO Guide to Boiler Failure Analysis* [6] includes photographs of chelant corrosion, very similar in appearance to that of the ruptured feedwater pipe described in this paper.

4. Failure analysis

Flow analyses confirmed that flow and pressure conditions are far from those necessary for cavitation and cavitation damage in this particular system. At no point does the fluid pressure approach that necessary for cavitation. The analysis did identify a recirculation zone along the trailing surface of the chemical feed quill, and this recirculation carries fluid from the tip of the quill toward its base at the pipe wall. Much of the corroded internal surface of the subject feed pipe has the distinctive wave-like appearance of flow-accelerated corrosion, and metallographic analyses found no evidence of the cold working that is characteristic of cavitation damage. Hence, the morphology and microstructure of the corroded surface suggest that the pipe wall loss was caused by flow-accelerated corrosion.

However, the location and extent of damage are inconsistent with flow-accelerated corrosion caused by moderate-pH, low-oxygen feedwater. In the absence of aggravating factors, flow-accelerated corrosion occurs where there is flow impingement, at or very close to flow changes, not well downstream of flow changes. For example, it occurs on the immediate downstream side of elbows and tees. In the subject piping, wastage occurred through a substantial length of straight piping while there was no damage in preceding elbows or at the base of the chelant feed quill.

Moreover, there was no damage in the immediately preceding pipe where there was a similar geometric sequence of an elbow (header-to-feedwater pipe) followed immediately by a thermocouple well having nearly the same geometry as the chelant feed quill. Hence, the feedwater was relatively non-corrosive at this earlier location but became corrosive just downstream of the chelant feed quill. Downstream of the feed quill, pipe wall corrosion continued along the full length of straight pipe, through the next pipe bend and some way up the vertical riser, where the corrosion ended abruptly.

The results of a Fourier transform infrared (FTIR) analysis revealed the existence of carbohydroxyl radicals in the ruptured area, which is indicative of chelants or organic polymers included in the commercial

chelant blends. FTIR analysis also indicated the absence of the same in the non-corroded area of the feedwater line either upstream or downstream of the chemical injection quill.

5. Wastage mechanism

The above observations indicate that pipe wall wastage prior to the pipe failure was caused by the chelant fed through the chemical feed quill into the flowing feedwater immediately upstream of the wastage area.

Wastage of the subject economizer-to-drum feedwater pipe was caused primarily by the immediate activity of the chelant product injected just upstream of the failure. The chelant fed through the chemical feed quill flowed to the pipewall where it contacted and reacted with the inner surface of the pipe in a clearly defined pattern. Like an acid, the chelant mixture is both oxidant and solvent. This combination produced the features characteristic of a flowing acid. Uncorroded plateaus protected by surface oxide are pocked with pits and abruptly give way to areas of severe wastage. Much of the wastage noted has the scalloped appearance of flow-accelerated corrosion. Other areas look gouged. During periods when conditions were less corrosive (e.g. because of lower chemical feed rates), some scalloped areas redeveloped protective surface oxides but subsequently pitted. Downstream, the wastage area ends abruptly where the corrodant is depleted and the protective surface oxide had yet to break down.

Corrosion is an electrochemical process. For iron to corrode, it must first lose electrons (oxidize) to form soluble ferrous ions, $Fe^o \rightarrow Fe^{+++}2e^-$. For the feedwater pipe to corrode, the feedwater must react with these electrons as well as carry away the dissolved iron. Net reactions for iron chelation are, for example:

$$Na_4(EDTA) + 2Fe^o + 4H_2O \rightarrow Fe_2(EDTA) + 4NaOH + 2H_2 \uparrow$$

Sodium EDTA (free chelant) + iron metal + water \rightarrow iron chelate + caustic + hydrogen gas (liberated).

This is similar to corrosion caused by acids, oxygen, and other organics. Acids are corrosive because they have a lot of hydrogen ions (H⁺) that take away electrons to form hydrogen gas, $2H^+ + 2e^- \rightarrow H_2$. Oxygen is corrosive because it takes away electrons to form hydroxyl ions, $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$. Similarly, organics can also be corrosive at high temperatures. For example, carboxylic groups can take away electrons to form aldehyde groups R-COOH + $2H^+ + 2e^- \rightarrow R$ -CHO + H_2O [7]. Because of this corrosive effect, long standing industry practice is to minimize boiler feedwater concentrations of acids, oxygen, and organics. However, for low-pressure (15–1000 psi) boilers, organic chelants and polymers are valuable tools for keeping deposit-forming minerals and oxides in solution or suspension.

The best technical support for this potential mechanism is a study by Palmer and Boden [7]. Corrosion rates were measured in static pH 9.0 solutions at $140-194^{\circ}F$ with EDTA concentrations from 29 to 2900 ppm (parts per million). The corrosion rate of steel in EDTA is cathodically (electron uptake) controlled by the reduction of EDTA, (e.g. reduction of carboxylic groups to aldehyde groups, R-COOH + $2H^+$ + $2e^- \rightarrow R$ -CHO + H_2O). The measured iron dissolution rate in 29 ppm EDTA solution at $176^{\circ}F$ was only about 9 mils per year (thousandths of an inch per year). However, the corrosion rate of steel increased by a factor of three as the temperature increased from 140 to $194^{\circ}F$. More rapid thermal decomposition at higher temperatures will greatly increase the cathodic reduction rate and thereby the corrosion rate.

6. Conclusions: why the failure in this boiler and not in others?

• After extensive investigation, the failure was attributed to flow-assisted chelant corrosion, which thinned the feedwater pipe wall from the inside surface to the point of rupture under normal operating conditions.

- Wastage in the subject boiler feedwater pipe was caused by periods of excessive chelant product injection into feedwater at temperatures where the chelant is exceptionally aggressive. There has been some wastage in other feedwater lines either at or just downstream from chemical feed quills, but the extent of wastage in the subject boiler was exceptional.
- For the subject boiler, the nominal economizer-to-drum feedwater temperature was about 414°F. Compared to similar 900 psi boilers with similar feedwater and boiler water temperatures, the subject boiler received relatively high concentrations of chelant-based treatment chemicals. At a pressure of 930 psi the boiler water saturation temperature is 540°F, but fluid/tube interface temperatures are somewhat higher in high heat flux areas so surface catalyzed decomposition of the chelant was especially rapid. The boiler operated with a free-chelant (unreacted) target concentration of 5–10 ppm. Free chelant decomposed rapidly within the boiler, especially in the higher heat-flux areas of furnace walls, and additional chelant product was periodically fed to the subject boiler in an effort to maintain the target free-chelant residual in the boiler water. As it was from the boiler water that samples were collected, and the chemical feed rates set, in fact the free-chelant target was often exceeded. Chelant overfeed may also have been exacerbated by periodic hardness excursions in the feedwater. Chelant feed was periodically increased to chelate excess hardness in the boiler water, though the feedwater hardness was not necessarily high at the time or did not remain high.

7. Recommendations

- Organic chelant-based additives to boiler water must be used with care because of their potential for causing corrosion, especially at higher pressures (e.g. 900 psi) where fluid and metal temperatures are higher.
- The risk of corrosion increases with temperature and, therefore, with increasing pressure. This means that with increasing operating pressures, there must be a corresponding increase in the level of care in application of chelant-based products.
- To ensure against overfeed of chelants, the chelant feed rate must be based on feedwater hardness, not residual boiler water chelant concentration, and the rate must be continuously adjusted as needed. This is an established practice for many boilers and is especially important at pressures approaching or exceeding 900 psig, where free-chelant decomposition is especially rapid. Use of chelants above 1000 psi is not recommended.
- Oxygen levels should be measured in the feedwater at least weekly, immediately after the deaerator and at a point just before the feedwater enters the steam drum. The level should be no higher than 7 ppb (parts per billion) with the oxygen scavenger turned off.
- Dissolved and total iron in the feedwater should be measured at the same frequency and locations as the oxygen. Any increase noted between these sample points is an indication that corrosion is probably occurring.
- Feedwater piping should be inspected at regular intervals, especially where pH is less than 9.5, chelant treatment is employed, or there is prior evidence of feedwater pipe wastage. Areas of particular concern are chelant and other chemical feed locations, bends, valves, tees and their immediate downstream areas. Ultrasonic methods can be used to measure pipe wall thickness. Inaccessible areas can be inspected visually using fiber optics or remote cameras. Corroded areas are generally roughened to the extent that they are easy to see with low angle lighting. EPRI [3] has developed software currently in use for establishing a piping system database, thus allowing for comparison over time. The software also has the capability to predict where FAC may be most likely to occur.
- If inspection measurements show that unacceptable rates or patterns of corrosion are occurring, then changes to materials and injection procedures should be considered so as to reduce the risk of failure.

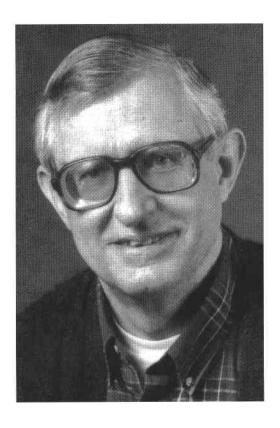
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ENGINEERING PROFESSOR WINS THE 2001ASME/ TRIODYNE SAFETY AWARD!



Dr. George W. Pearsall

Triodyne is delighted to announce that Dr. George W. Pearsall is the 2001 recipient of the ASME-Triodyne Safety Award.

Dr. Pearsall is Professor of Mechanical Engineering and Materials Science and Professor of Public Policy Studies at Duke University (since 1964) and has twice served as Duke's Dean of the School of Engineering. Dr. Pearsall earned his Bachelor of Metallurgical Engineering from Rensselaer Polytechnic Institute of Technology and his Doctor of Science degree from Massachusetts Institute of Technology. He is a licensed Professional Engineer in the State of North Carolina.

Throughout his career, Dr. Pearsall has focused his teaching and research on safe product design, the ethical obligations of engineers and the public policy implications of technology. He created and taught courses like Ethics and the Professions, Ethics and Technology, Safe Product

Design, Analytical Methods for Public Policy Making, Failure Analysis and Prevention, Product Safety and Design, and Materials, Failure, Risk and Society. Dr. Pearsall's research concentrates on failure analysis in relation to product safety and design. His current focus is fracture characteristics of polycarbonate and other engineering plastics. His research techniques include optical microscopy, scanning electron microscopy, and scanning tunneling electron microscopy to characterize and record the various ways in which the fracture surfaces of polycarbonate and other plastics exhibit fine-scale banding (superficially resembling fatigue striations) when the fracture is brittle and the stress has no cyclic components. These bands occur in a variety of different microscopic forms and exhibit morphological details that are major subjects of this research. They provide extremely reliable indicators of the crack's direction and state of stress when the bands were formed.

Dr. Pearsall has conducted failure analyses on many products including a collapsed tower crane, a heart catheter guide wire, fiberglass motorcycle helmets, silicon breast implants, pool toys, polystyrene toilet seats and heart pacemaker lead insulation.

In 1979 Dr. Pearsall established the Duke-IBM Product Safety Institute, which for the next ten years trained hundreds of IBM product-safety engineers and product managers in safety concepts and techniques. He taught similar concepts at Motorola and in Japan.

Dr. Pearsall is especially proud of the fact that many of his former students are design engineers or consultants with significant responsibility for safety in the biggest corporations in the world.

Professor Pearsall's recent publications include:

"Variations in Two-Point Discrimination as a Function of Terminal Probes," Microsurgery, 1989, with L. S. Levin, N. Regan, and J. A. Nunley.

"Study of the Fracture Toughness and Fracture Morphology of Polybenzimidazole," J. of Materials Science, 1992, with J. F. Groves and C. M. Agrawal.

"Application of Scanning Tunneling Microscopy to the Study of Fracture Morphology of Polycarbonate," J. of Materials Science, 1992, with C. M. Agrawal, K. Hunter, and R. W. Henkens.

NOMINATIONS FOR THE 2003 ASME-TRIODYNE SAFETY AWARD ARE NOW OPEN!

ELIGIBILITY

The American Society of Mechanical Engineers' ASME-Triodyne Safety award is presented to either educators or practitioners who have made significant contributions to teaching, research or practice in the safety aspects of mechanical design.

AWARD DESCRIPTION

The recipient of the ASME-Triodyne Safety Award receives a plaque to commemorate his/her achievements, and an honorarium of \$1000, plus expenses to cover travel and accommodations for the presentation of the award. The award is administered by the Design Education Committee of the ASME Design Engineering Division and is presented at a special function during the ASME International Mechanical Engineering Congress and Exhibition.

HOW ARE CANDIDATES SELECTED?

Nominations for the 2003 ASME-Triodyne Safety Award are now open. The first step in the selection process is to obtain and then complete the nomination forms. Nominating forms can be obtained from:

Professor Tai-Ran Hsu
Department of Mechanical & Aerospace Engineering
San Jose State University
One Washington Square
San Jose, CA 95192-0087
e-mail: tairan@email.sisu.edu

After the completed forms have been received the selection committee chaired by Professor Tai-Ran and consisting of a member of the ASME Safety Division, a former award recipient and two members of the ASME Design Education Committee, reviews the nominations and makes the selection. Triodyne, Inc does not participate in the selection process.

The closing date for the 2003 nominations is March 29, 2003.



SAFETY BRIEF

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