THE MASSACHUSETTS
TOXICS USE REDUCTION INSTITUTE

RIVERDALE MILLS CORPORATION
NORTHBRIDGE, MASSACHUSETTS

ELIMINATION OF ACID AND LEAD IN WIRE STRAND ANNEALING AND GALVANIZING

TOXICS USE REDUCTION INSTITUTE
CLEANER TECHNOLOGY
DEMONSTRATION SITES PROGRAM

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University of Massachusetts Lowell

Riverdale Mills Corporation
Northbridge, Massachusetts

Elimination of Acid and Lead in Wire Strand Annealing and Galvanizing

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The Toxics Use Reduction Institute
Cleaner Technology Demonstration Sites Program

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The Toxics Use Reduction Institute is a multi-disciplinary research, education, and policy center established by the Massachusetts Toxics Use Reduction Act of 1989. The Institute sponsors and conducts research, organizes education and training programs, and provides technical support to promote the reduction in the use of toxic chemicals or the generation of toxic chemical byproducts in industry and commerce. Further information can be obtained by writing the Toxics Use Reduction Institute, University of Massachusetts Lowell, One University Avenue, Lowell, Massachusetts 01854.

PREFACE

The Massachusetts Toxics Use Reduction Institute annually provides direct funding to Massachusetts industries to facilitate the development, use and demonstration of innovative techniques that reduce the use of toxic chemicals or the generation of toxic by-products.

In its 1993 fiscal year, the Institute initiated the Industry Matching Grants Program, which provided funding on a matching basis for toxics use reduction (TUR) feasibility and technology studies. Grants were awarded on a competitive basis for companies to conduct TUR studies at their facilities. Grant recipients prepared project reports which assisted in transferring toxics use reduction technologies and methods to other companies.

In its 1996 fiscal year, the Institute launched the Cleaner Technology Demonstration Sites Program. The goal of the program was to promote the adoption of cleaner technologies by Massachusetts industry. Five companies were selected as demonstration sites to showcase the implementation of technologies that embrace the concepts and principles of toxics use reduction. The program, which included a series of visits to the facilities and related presentations and publications, allowed individuals and firms to observe and assess their value first-hand. Site visits were open to industry, environmental groups, community groups, the media and others.

In its 1997 fiscal year, the programs were combined where funding could be obtained either for feasibility studies or for demonstrations.

Associate sponsors of the 1999-2000 Demonstration Sites and Matching Grants Program included the Massachusetts Office of Technical Assistance for Toxics Use Reduction, the Massachusetts Executive Office of Environmental Affairs, and the Massachusetts Department of Environmental Protection.

The following report is an in-depth analysis of the cleaner technology demonstrated at Riverdale Mills Corporation in Northbridge, Massachusetts. Karen Thomas edited the report.

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1.0 INTRODUCTION

Located in Northbridge, Massachusetts, Riverdale Mills Corporation employs 119 people and manufactures welded wire mesh products in its approximately 265,000 ft^2 facility. The wire mesh products are used in a wide range of customized and general purpose applications, specifically in marine (crab and lobster traps), land management (Gabions for erosion control), agriculture (wire slats used in poultry barns) and security fencing products. Riverdale Mills Corp. is an ISO 9002-94 registered welded wire products facility and was the recipient of the 1999 Governor's Award for Toxic Use Reduction. This Demonstration project is just one example of Riverdale's commitment to toxics use reduction.[1]

Requiring the addition of a new multi-wire strand galvanizing line to meet growing market demand, Riverdale Mills made the goals of toxics use reduction a large part of the operational requirements of the new line. The company sought to reduce or eliminate the chemicals conventionally used in the process, the byproducts generated and the energy required. These goals required the innovative re-thinking of a mature industrial process.

Riverdale Mills chose an induction heating chamber for the annealing process, eliminating the use of lead in the conventional liquid lead annealing process. Following annealing, commercial hot-dip wire galvanizing operations typically use hydrochloric acid in a pickling process, and zinc ammonium chloride as a flux prior to immersion into the zinc bath. Modifying the annealing process and annealing within an inert atmosphere replaced both the pickling and the flux processes; these were replaced by an alkaline soap pre-wash and hot water rinse. Re-engineering the process to eliminate the need to re-heat the wire during processing achieved significant energy savings.

Conservative estimates of savings, based on 80% utilization of the galvanizing capacity of the new line, show a reduction of 43,000 lb/year of hydrochloric acid and 25,000 lb/year of zinc ammonium chloride, or 100% reductions, from the conventional process. The new process also eliminates the use of lead. Massachusetts Electric Company has estimated savings of up to 1.2 million kWH per year. For their innovative work on this project, Riverdale Mills Corp. was recognized by Massachusetts Electric as a Design 2000 Energy Efficient Project.[2]

The process, which is pending patent, is set to revolutionize the wire strand industry with its monetary as well as environmental benefits.

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[1] For a list of previous projects, see Appendix A.

[2] See Appendix B for more information on Design 2000, a Massachusetts Electric project.

2.0 DESCRIPTION OF CONVENTIONAL PROCESS

Figure 1 shows a conventional galvanizing operation sequence along with the process temperatures.

Prior to the galvanizing process, the wire is drawn. Wire drawing is the process by which wires are reduced in size when drawn through carbide dies. Beginning as a bar or rod (7/32 inches in diameter), the wire is drawn to smaller sizes such as intermediate wire, fine wire and ultrafine wire.

In order to facilitate the drawing of wire at high speeds, a process that causes an increase in the wire temperature and can cause sticking of the wire to the die surface, the wire is passed through a dry powdered lubricant. Dry drawing lubricants are commonly calcium or sodium stearates with additives. These lubricants must be cleaned off prior to further processing.

The drawing process results in tensile pulling of the wire, which produces residual stresses and increases its temperature. These stresses can cause distortions in the wire, cracking, and embrittlement of the wire, which could result in premature breakage in service. To overcome these deficiencies the wire is heated above its re-crystallization temperature to allow the metal grains to reform and relieve the stress; this process is called annealing. To protect from oxidation, which would affect the mechanical and physical properties, the wire is galvanized.

2.1 Annealing

Annealing is a heat treatment in which a material is exposed to an elevated temperature for an extended time period and then slowly cooled. It is the process by which glass, metals, and other materials are treated to render them less brittle and more workable. Annealing provides the following benefits to the material:

- Relieves stresses
- Increases softness, ductility and toughness
- Produces a specific microstructure or homogenizes the existing microstructure
- Improves machinability, electrical properties, dimensional stability and formability for cold working, such as cold heading and stamping

Annealing heat treatments are mostly characterized by the induced micro structural changes that are ultimately responsible for the alteration of the materials' mechanical properties. Any annealing process consists of three stages:

- Heating to the desired temperature
- Holding or "soaking" at that temperature
- Cooling, usually to room temperature

During these three steps, time is very important. During heating and cooling, there exist temperature gradients between the outside and the interior portions of the piece. If the rate of temperature change is too great, temperature gradients and internal stresses may lead to warping or cracking. In addition, the actual annealing time must be long enough to allow for any necessary transformations to take place.

In the conventional annealing process for steel wire, the wire is dipped in a bath of liquid lead, usually gas-heated to 1300-1400°F. Upon exiting the lead bath, charcoal is used as a wiping media to reduce the amount of lead carried out on the wire and to minimize wire surface oxidation. (More recently, fluidized bed furnaces have been used for annealing. In these furnaces a mixture air and natural gas is ignited and percolated through a sand bed. The sand becomes fluid due to the bubbling effect of burning natural gas and the wire is pulled through this heated media. This section will discuss the older molten lead process.)

2.2 Quenching, Acid Pickling and Flux Application

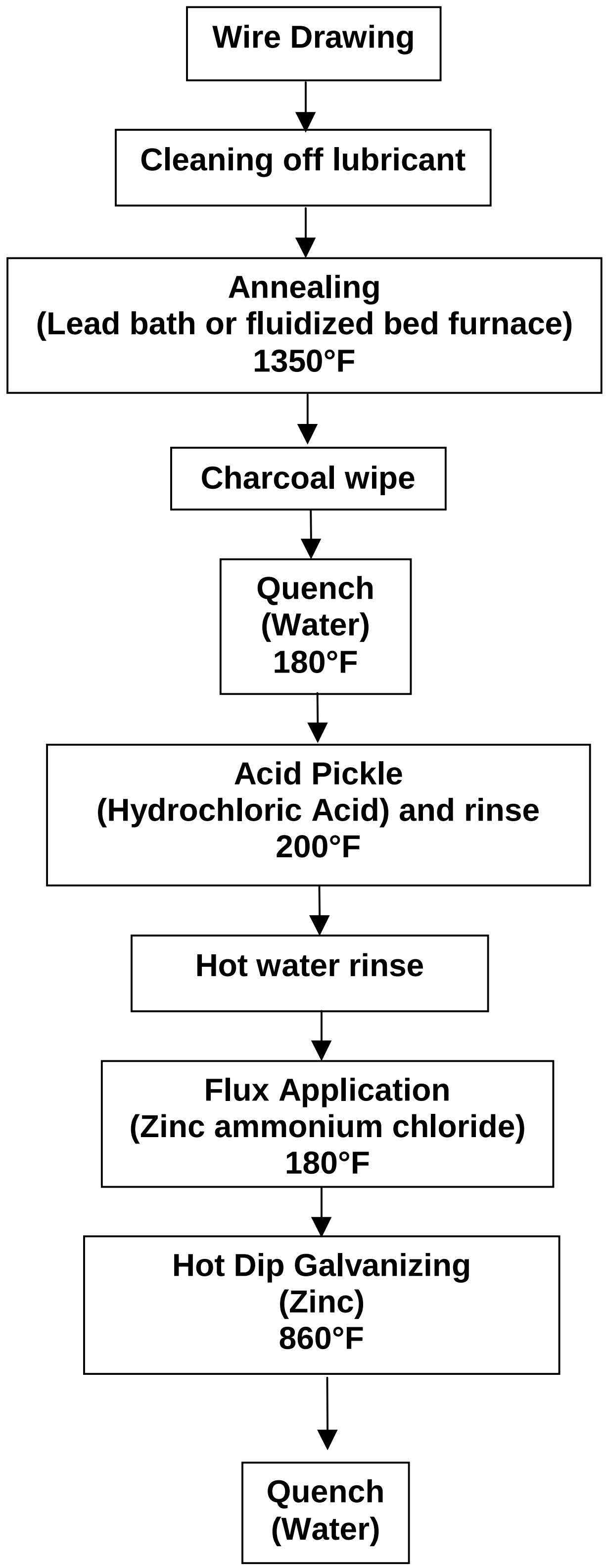
After the annealing process, the wire is quenched in a water bath. This step is necessary to prevent overheating of the acid bath, the next step in the process.

In the acid pickling step, the wire is passed through a hydrochloric acid solution. Pickling serves two purposes. It removes oxides resulting from the hot wire being exposed to oxygen and it removes any remaining lead coating on the wire from the molten lead bath. These contaminants must be removed or they will interfere with the zinc galvanizing process.

On passing the wire through the hydrochloric acid bath, the acid reacts with any remaining lead to form lead chloride. The lead chloride is a byproduct from the process and must be disposed of properly. In addition, the hydrochloric acid baths must be discarded periodically when they have become contaminated. Any remaining traces of acid are then removed by rinsing the wire with hot water. The rinsing process is a multi-tank, counter-flow, hot water rinse system. The counter flow is necessary to ensure that the water in the last tank remains relatively clean and free of contaminants. The water must be kept hot to minimize both the process time and the potential for surface oxide formation. The rinsing process results in acidic wastewater that must be neutralized prior to disposal.

Subsequently, the wire is dipped in a flux bath, usually a zinc ammonium chloride solution. Flux is an anti-oxidant, dissolving any residual oxides and preventing further oxidation of the surface prior to galvanizing. Any oxidized or contaminated area on the wire can cause poor adhesion of the zinc coating in the galvanizing process, leading to black spots and flaking. The flux does not cause adhesion of zinc and steel (as in the galvanizing step) but only compensates for inadequate cleaning.

Figure 1: Conventional Annealing and Galvanizing Operation Sequence



2.3 Hot Dip Galvanizing

Galvanizing is the practice of immersing clean, oxide-free iron or steel into molten zinc at about 860°F (above the melting temperature of 780°F) in order to form a zinc coating that is metallurgically bonded to the iron or steel surface. In the U.S. approximately 1 million metric tons of zinc is used annually, primarily to protect iron and steel from corrosion. The zinc coating protects the surface against corrosion, oxidation and moisture in two ways: 1) it shields the base metal from the atmosphere; 2) the zinc provides anodic (or sacrificial) protection. (The attack of corrosive agents is first on the zinc coating before it affects the underlying metal. Because zinc is more electronegative than iron or steel, even when the surface is scratched and the base metal is exposed, the zinc is slowly consumed while the iron or steel remains protected from corrosion. The zinc protects the steel "galvanically," giving the process its name.)

When the steel is dipped in the zinc bath it heats up to above the melting temperature and a zinc iron reaction occurs, creating several layers of inter-metallic alloys that bond the outer layer of pure zinc to the steel. The reaction can only occur if the iron in the steel is in intimate contact with the liquid zinc. Any surface contamination will impair this reaction. The cleanliness of the surface is thus of absolute importance and is critical in achieving a proper and consistent coating.

Following the zinc hot dip, the wire is quenched in water to "freeze" the zinc layer and is then coiled or spooled.

The hot dip galvanizing process is adaptable to coating nearly all types of fabricated and non-fabricated products such as wire, tanks, sheets, strip, pipes and tubes, fittings, hardware, wire cloth, hollow-ware, and structural assemblies.

3.0 DESCRIPTION OF CLEANER TECHNOLOGY

The galvanizing process designed using the concepts of cleaner production and toxics use reduction performs the annealing step without lead and in an inert atmosphere, which eliminate the need for acid pickling. Figure 2 shows the steps involved in the Cleaner Technology Galvanizing process.

This new technology requires a cleaning step at the beginning of the sequence. Riverdale Mills uses a sodium hydroxide aqueous cleaner which contains caustic soda along with emulsifiers, water softeners and wetting agents. A pump with a filtration unit continuously recirculates the solution from the lower holding tank into the upper dip baths. The solution in the holding tank is heated with electric heaters to around 200°F. The wire is immersed in the heated solution and then passed through a second solution bath containing ultrasonic transducers. The ultrasonic energy aids in removing any remaining particles from the wire surface.

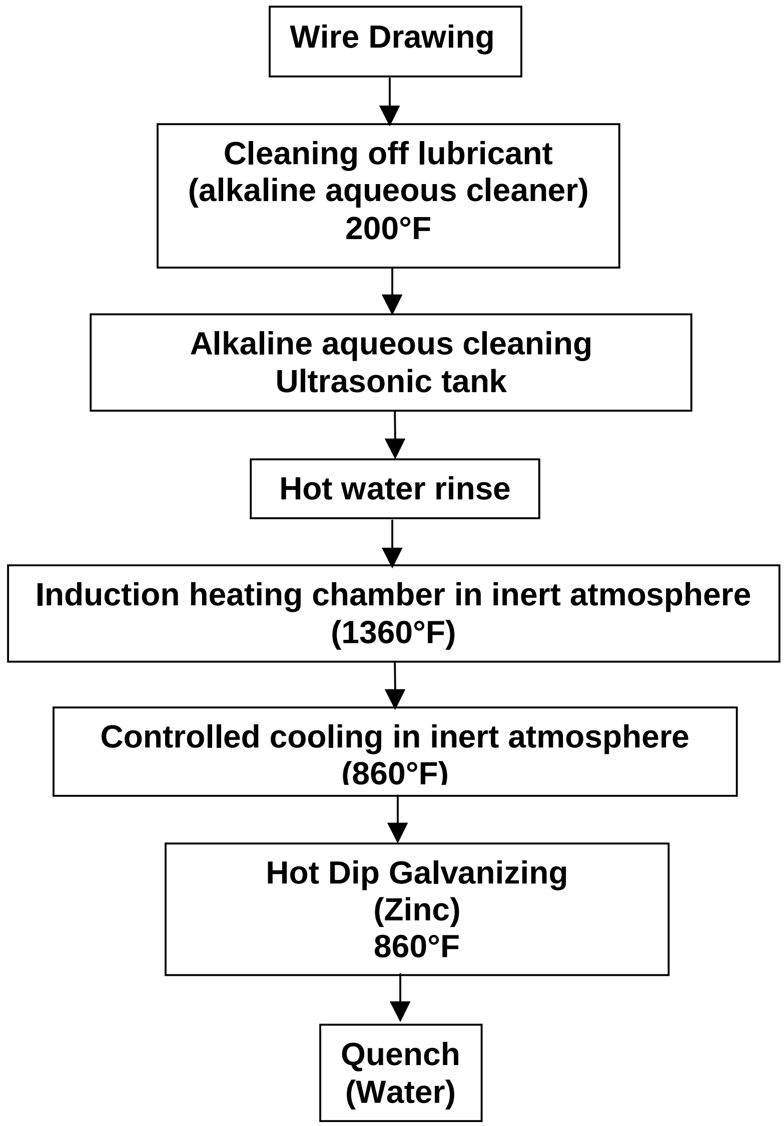
The wire is then rinsed in hot water to remove any remaining alkaline solution or soap particles from the previous washing step. The wire is passed through a three-chambered, counter-flow rinse tank filled with the hot water. Clean water is introduced into the last tank, creating a cascade of water through the three tanks and it finally overflows into a catch basin. Once the alkaline bath is spent, it is mixed with acidic wastewater from another process (unrelated to the strand galvanizing line), where it is used to aid in neutralization.

After cleaning, the wire is passed through an inclined induction-heating chamber, which helps to remove any residual stresses from the drawing process. The induction chamber heats the wire by passing it through a strong electro-magnetic field. The heat treatment is carried out under a reducing atmosphere of nitrogen and hydrogen. Keeping a positive pressure throughout the process and thus preventing ambient air from entering the furnace maintain the inert atmosphere. The wire remains in this inert atmosphere throughout the process from this point. The inert gas eliminates any contact with atmospheric oxygen, preventing oxide formation on the wire surface and the hydrogen reacts with any oxides or impurities on the wire and removes them. The wire exits the annealing process completely clean and oxide-free.

In the induction-heating chamber, the wire is passed through the first heating chamber and heated to a temperature of 1360°F, which helps bring a phase transformation in the wire. The wire is then cooled under controlled conditions to the galvanizing conditions at about 860°F. The cooling is done using fans which pump the inert gas on the wire and the fan speeds are adjusted using PLC controller to maintain an exit wire temperature of 860°F, which is the temperature of the pot/molten zinc. A heat exchanger cools the gas if the wire gets too hot. Although zinc melts at 760^{O}F, the wire is heated to 860^{O}F to facilitate its reaction with the zinc solution.

Finally the hot wire is immersed into the molten zinc pot, which coats the wire completely with a protective layer of zinc and protects it against oxide formation. The wire is then quenched and coiled or spooled.

Figure 2: Cleaner Technology Wire Strand Galvanizing Process



4.0 TOXIC USE REDUCTION ASSESSMENT

4.1 Environmental Assessment

By choosing to design the new process with environmental considerations in mind, Riverdale Mills was able to eliminate both the acid pickling and flux application steps in the wire strand galvanizing process. The new design eliminates an estimated 43,000 lbs/year of hydrochloric acid and 25,000 lbs/year of zinc ammonium chloride. The disposal of spent acid and metallic sludge, and the neutralization process for the acidic rinse water are also eliminated. In addition, by choosing an induction heating process, Riverdale Mills avoided the use of a significant amount of lead, approximately 100,000 pounds per year.

Substantial energy savings were a result of this redesign. In a conventional galvanizing line the wire has to be re-heated in the zinc bath in order for proper galvanizing to take place. With the acid pickling and flux application steps eliminated, and by retaining the heat in the wire from the annealing furnace, it is not necessary to re-heat the wire. In addition, this allows for a smaller zinc furnace, reducing the radiant heat losses from the zinc surface. The induction heating process also has the ability to be shut off when not in use as opposed to the lead annealing process which must be kept running continuously. Massachusetts Electric has estimated an overall savings as a result of process redesign of 1.2 million kWH per year or 50% of the conventional process.

See Table 1 for a toxics use reduction comparison of the conventional and new processes.

Table 1. Summary of Toxics Use Reduction for Conventional and Redesigned Wire Strand Galvanizing Processes

	Conventional Process	New Process
Hydrochloric Acid (pounds/yr)	43,000	0
Lead (pounds)	100,000 initially 35,000 annually	0
Ammonium zinc chloride (pounds/yr)	25,000	0
Energy (kWH/yr)	2.4 million	1.2 million

Notes: Data for chemical use (except lead) are based on 80% utilization of galvanizing capacity (21,000 tons/year capacity). Data for energy use are based on continuous operation of process. The amount of lead used in a conventional process is a rough approximation based on a similarly sized gas-fired galvanizing process.

Table 2 shows a summary of the resulting wastes from both the conventional and redesigned wire strand galvanizing processes.

Table 2. Summary of Wastes for Conventional and Redesigned Wire Strand Galvanizing Processes

Conventional Process	New Process
Spent Hydrochloric Acid Metallic sludge (containing lead) Acidic rinsewater Ash, top-dross and bottom dross (returned to zinc smelters)	Spent alkaline wash water Alkaline rinse water Ash, top-dross and bottom dross (returned to zinc smelters)

4.2 Occupational Health and Safety Assessment

The new process for wire strand galvanizing eliminates the potential worker exposure to hydrochloric acid, lead and zinc ammonium chloride.

Hydrochloric acid is a corrosive irritant to the skin, eyes and mucous membranes. It is toxic to humans by inhalation and experimentally by ingestion. It is an experimental teratogen and mutation data has been reported.

Lead is a probable teratogen, probable developmental hazard and possible carcinogen. In industry the greatest risk of exposure is due to inhalation of dust, fumes and vapors. The major organ systems affected by lead are the nervous system, blood system and kidneys.

Zinc ammonium chloride is an irritant. Inhalation of zinc ammonium chloride dust may irritate the nose and throat. Ingestion can cause irritation or corrosion of the alimentary tract. Contact with eyes or skin causes irritation.

Due to the redesign of this process, workers at Riverdale Mills will not be put at risk of being exposed to these health hazards.

4.3 Economic Benefits

Although not quantified, cost savings associated with the new design follow:

- Chemical purchases
  It is not necessary to purchase hydrochloric acid, zinc ammonium chloride or lead

- Waste treatment chemical purchases
  Neutralization of acidic rinse water is not required.

- Waste disposal
  Metallic sludges are not produced and do not have to be disposed

- Regulatory fees and associated paperwork
  Hydrochloric acid, lead and zinc ammonium chloride are on the TURA list of toxic and hazardous chemicals and thus require fees over certain thresholds of use. [3] Reporting for lead and hydrochloric acid (acid aerosols) emissions is required under the Toxic Chemical Release Inventory.[4]

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[3] Annual fees are required under the Massachusetts Toxics Use Reduction Act for chemicals appearing on the TURA list of Toxic and Hazardous Chemicals for Massachusetts companies that employed at least 10 full-time employees, manufactured in one of the covered SIC codes (10-14, 20-39, 40, 44-51, 72, 73, 75, 76), and were a large quantity toxics user. For a complete description, refer to the Mass. Department of Environmental Protection (DEP) website at http://www.state.ma.us/dep/bwp/dhm/tura/turapubs.htm, or

- Labor and time
  Fewer process steps requires less labor and less processing time

- Electricity
  New process uses 1.2 million kWH less electricity

request a copy of the 1999 Form S Reporting Package from the DEP Infoline at (617) 338-2255 or 1-800-462-0444.

[4] Refer to the website of the Environmental Protection Agency at http://www.epa.gov/tri/ or phone the Emergency Planning and Community Right-To-Know Act Hotline at (800) 424-9346.

REFERENCES

Boyer, Howard E. and Timothy L. Gall, editors "Metals Handbook" (American Society for Metals: Metals Park, OH), 1985.

Lewis, Richard J., "Hazardous Chemicals Desk Reference, 3rd Edition" (Van Nostrand Reinhold: New York), 1993.

APPENDIX A

Following is a list of previous toxics use reduction projects undertaken by Riverdale Mills:

- Plastic coating without solvents
- Water-based adhesives for adhering plastic coatings to metallic substrates
- Ceramic zinc kettles to minimize the production of waste zinc-iron alloys in conventional iron kettles
- Use of hydro-electric power and natural gas fired diesel engines
- Mechanical removal of iron-oxide scale from steel rod instead of using acid

APPENDIX B

See http://www.masselectric.com/cust/bus/effic/2000/index.htm