

Pollution Prevention Technology Profile

Trivalent Chromium Replacements for Hexavalent Chromium Plating

November 18, 2003

Introduction

The purpose of this Technology Profile is to provide general information about trivalent chromium plating as a replacement for hexavalent chromium plating. Trivalent chromium is also known as tri-chrome, Cr^{+3} , and chrome (III), whereas hexavalent chromium is also known as hex-chrome, Cr^{+6} , and chrome (VI). The Profile has the following sections:

- Chromium Plating Overview
 - Hexavalent Chromium Technology
 - Regulatory Requirements
 - Non-Chromium Alternatives
- Trivalent Chromium Technology
 - P2 for Trivalent Chromium Baths
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- Benefits and Challenges
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It should be noted that this Technology Profile is not intended to be an “approval” of this technology. The appropriateness of the use of trivalent chromium plating technologies should be determined on a site-by-site basis. Potential users should contact officials in the state in which the facility is located to determine the state-specific regulatory requirements that could apply. A listing of state contacts is located at the end of this Profile.

Chromium Plating Overview

The most common hexavalent chromium-bearing solutions include decorative and hard chromium, aluminum conversion coating, bright dipping of copper and copper alloys, chromic acid anodizing, and chromate conversion coatings on cadmium, zinc, silver and copper. This Technology Profile is for the use of trivalent chromium processes as replacements for decorative and hard hexavalent chromium processes.

Decorative Chromium

Decorative chromium plating provides a durable coating with a pleasing appearance and is usually deposited in a thickness range of 0.002 to 0.020 mils. It is most often applied over a bright nickel-plated deposit, which is usually deposited on substrates such as steel, aluminum, plastic, copper alloys and zinc die casting. Decorative chromium plating typically ranges from 0.005 mils to 0.01 mils in thickness. Common items with decorative chrome include appliances, jewelry, plastic knobs, hardware, hand tools, and automotive trim.

Hard Chromium

When chromium is applied for any other purpose, or when appearance is a lesser feature, the process is commonly referred to as hard chromium plating, or functional chromium plating. Hard chromium plating typically ranges from 0.1 to 10 mils thickness. Common applications of functional plating include: hydraulic cylinders and rods, crankshafts, printing plates/rolls, pistons for internal combustion engines, molds for plastic and fiberglass parts manufacture, and cutting tools. Functional chromium is commonly specified for rebuilding worn parts such as rolls, molding dies, cylinder liners, and crankshafts.

Chromium plating provides excellent hardness (typically 700-1,000 Vickers), bright appearance with no discoloration, and resistance to corrosive environments; it is easily applied and has a low cost. However, hexavalent chromium plating suffers from low cathode efficiency, poor metal distribution, lack of coverage around holes, and is very difficult to use in barrel plating. It is also a worker- and environment-unfriendly process. Some of the most important parameters for evaluating the effectiveness of chromium plating include: plating thickness, hardness, plating rate, and cathode efficiency.

Hexavalent Chromium Plating Technology

In the traditional hexavalent chrome plating process, the process steps are generally:

activation bath ? chromium bath ? rinse 1 ? rinse 2

The activation bath, if used, is a separate tank of chromic acid. The activation step is typically (depending on the alloy) a reverse current etch to prepare the surface of the parts to accept the plating by removing oxides from the surface of the material. Sometimes the activation step takes place in the chromium bath itself.

The composition of the chromium bath is chromic acid (CrO_3) and sulfate (SO_4), with ratios ranging from 75:1 to 250:1 by weight. The bath is extremely acidic with a pH of 0. The bath may be co-catalyzed with fluorides. In the chromic acid, the chromium is in the +6 oxidation state, which is reduced to Cr^{+3} , then to unstable Cr^{+2} and finally to Cr^0 . Some Cr^{+3} is necessary in the bath to act as a reducing agent, however, concentrations of Cr^{+3} exceeding 2-3% of the chromic acid content can cause problems. (Many specifications require that this concentration not exceed 1%). The presence of other oxides of metals (e.g., iron, copper, nickel) combined with the Cr^{+3} hinders bath performance.

In addition to bath composition, the other important parameters are temperature and current density. Together, these affect brightness and coverage. Generally, bath temperatures for decorative coating range from 95 to 115°F and 120 to 150°F for hard coating. Generally, the higher the current density is, the higher the temperature requirement. Current density also affects cathode efficiency. Agitation of the bath is required to equalize the bath temperature and promote uniform brightness on the part. Preheating the parts to be plated by placing them in the solution without current applied, may be necessary to obtain a uniform deposit.

The low cathode efficiency of the hexavalent chromium results in the major issue with chromium plating: poor coverage in low current density areas, and excessive build-up in high current density areas (e.g. part edges). The ability of a coating to cover the part uniformly is referred to as “throwing power.” In many cases, the part is over-plated, and ground back to final dimensions. In other cases, auxiliary anodes are used to provide more uniform coating of the part.

Regulatory Requirements

The principal ingredient in hexavalent chromium plating solutions is chromium trioxide (chromic acid). Chromium trioxide contains approximately 52% hexavalent chromium. Baths typically contain 28-32 ounces of hexavalent chromium per gallon. The hexavalent oxidation state is the most toxic form of chromium which has led to it being identified by the U.S. Environmental Protection Agency (EPA) as one of 17 “high priority” toxic chemicals for voluntary reduction through the 33/50 Program.

Air

Hexavalent chromium is a known human carcinogen and is listed as a hazardous air pollutant (HAP). Due to low cathode efficiency and high solution viscosity, hydrogen and oxygen bubbles are produced during the plating process, forming a mist of water and entrained hexavalent chromium. This mist is regulated under the Clean Air Act Amendments of 1990 and the Occupational Safety and Health Act of 1970.

On January 25, 1995, EPA published the Final Rule for its "National Emission Standards for Hard and Decorative Chromium Electroplating and Chromium Anodizing Tanks" (40 CFR Parts 9 and 63). EPA recently reduced the emission standards for chromium from 0.05 mg/m³ to 0.03 - 0.010 mg/m³, depending on the process, size of tank, and mist elimination technologies used. If a facility is using a trivalent chromium process for decorative plating, there is no emission standard; only recordkeeping and reporting requirements apply.

The Occupational Safety and Health Administration (OSHA) is scheduled to propose a new rule on hexavalent chromium compounds by October 10, 2004. The current permissible exposure limit, ceiling concentration, is 100 ug/m³.

Water

Chromium air emissions are frequently controlled by wet scrubbers. The discharge of these systems is treated with other process wastewaters. Wastewater that contains hexavalent chromium is treated first by acidification to 2.5 pH. This is followed by reduction of the hexavalent chromium to trivalent chromium using sulfur dioxide or sodium bisulfite. Finally, the solution is neutralized to precipitate the chromium as chromium hydroxide. Typical discharge concentrations for hexavalent and/or total chromium in wastewater are 0.1 to 1.0 ppm.

The EPA regulates chromium as a “priority pollutant” under the Clean Water Act. Under the Safe Drinking Water Act, a maximum contaminant level (MCL) is set for chromium at 0.1 parts per million (or 0.05 milligram/liter). The MCL is the maximum permissible level of a contaminant in drinking water from a public water system.

Waste

Under the Resource Conservation and Recovery Act (RCRA), chromium is a “hazardous constituent” and is a hazardous waste by toxicity characteristic if the concentration exceeds 5 mg/L (D007). Spent chromium plating baths are handled as hazardous waste. Precipitated chromium hydroxide sludges are regulated as F006 hazardous waste. For each pound of chromium that is lost to the waste treatment operations, 9.5 pounds of sludge (35% solids) are created.

In addition, lead anodes are typically used in hexavalent chromium plating. These anodes decompose over time, forming lead chromates, which slough off the anodes and deposit in the tank as lead chromate sludge that must be removed from the tank by filtering or pumping and disposed of as hazardous waste.

Hexavalent chromium plating solutions are typically treated with barium compounds to control the sulfate concentration by forming barium sulfate. This must also be disposed of as hazardous waste.

Right-to-Know Act

Under the Emergency Planning and Community Right-to-Know Act, Toxics Release Inventory (TRI) program, all large quantity (10,000 pounds/year) users of chromium must submit data on chromium releases and transfers.

Superfund

Under the Comprehensive Environmental Responsibility, Compensation and Liability Act (CERCLA, better known as Superfund), chromium is a “hazardous substance.” Users are liable for damages resulting from a release to the environment that occurs during past use or disposal practices. A company remains liable for its waste forever, even if the release to the environment occurs off-site at licensed disposal facility.

International

The European Union has adopted the End-of-Life Vehicle Directive in order to address the waste associated with vehicles at the end of their useful lives. The Directive aims to ensure the reuse, recycling

and recovery of end-of-life vehicles and their components. Hexavalent chromium is identified in the Directive as one of the hazardous materials used in the manufacture of vehicles. As such, it is banned from use in the manufacture of vehicles in the European Union nation states on July 1, 2003. This Directive is creating additional incentives for U.S. manufacturers to seek out alternatives to hexavalent chromium.

Non-Chromium Alternatives to Hexavalent Chromium

Due to increasing environmental and worker health concerns, some companies are seeking non-chromium alternatives for hard and decorative chromium applications. While non-chromium alternatives are not the focus of this Profile, limited information on some non-chromium alternatives is presented here.

The following table offers a summary of some of the non-chromium replacements for hard and decorative chromium baths. Many of the replacements are based on nickel which is also on EPA's list of 17 high priority chemicals for voluntary reduction through the 33/50 Program, along with chromium. Due to its complex mix of properties, no single coating will replace hexavalent chromium in all applications. Substitute coatings should be chosen based on the most important properties for each application. Solution trade names and manufacturers are included so that additional information can be obtained as needed. However, mention of any company, process, or product name should not be considered an endorsement by NEWMOA, NEWMOA member states, or U.S. EPA.

Table 1: Summary of Non-Chromium Substitutes for Hard and Decorative Chromium Baths

	Possible Non-Chromium Replacement	Notes	Vendor, Product
Electroplated nickel	Nickel-tungsten-boron	Uses conventional plating equipment and operates similar to a conventional nickel plating bath; may be more costly than hex chrome	AMPLATE
	Nickel-tungsten-silicon-carbide	May provide higher plating rates and higher cathode current efficiencies; may provide better throwing power and better wear resistance; may be more costly than hex chrome	Takada Inc.
	Tin-nickel	Good corrosion resistance in strong acids, breaks down above 320C, less wear resistance than hex chrome	
	Nickel-iron-cobalt	Vendor claims twice the wear resistance and 2.6 times the corrosion resistance of hex chrome; same color can be obtained	Shining Surface Systems, METTEX 6 (http://www.surface-systems.com/presentation_6.html),
	Nickel-tungsten-cobalt	Contains no chloride or strong chelators; can be used in rack and barrel plating; good corrosion resistance except in marine environments; may tarnish; contains ammonia	Enthone, Enloy Ni-150 (http://www.afonline.com/articles/00sum03.html)
Non-nickel electroplate	Tin-cobalt	Plate on nickel; decorative only	Seaboard Metal Finishing, Seachrome www.seaboardmetalfin.com
		Plate on decorative nickel and nickel alloy; may be used in racking; mildly alkaline	Enthone, Achrolyte
		Great color, light blue cast; no ammonia; no fluorides; no chlorides	MacDermid, CROMVET
	Cobalt Phosphorous	Nano-crystalline deposit produces extreme hardness; Plating current waveform modification (electrically mediated deposition) used to produce nanocrystalline deposit.	Integran Technologies, Inc. http://www.integran.com/
Electroless	Electroless nickel -nickel-tungsten -nickel-boron -nickel-diamond composite -nickel-phosphorous -nickel-polytetrafluorethylene	Possibly less hardness and abrasion resistance than hex; no build up on corners	Abrite, Millenium series, www.abrite.com MacDermid, NiKlad Sirius Surface Technology Micro Surface Corp.
Other Methods	HVOF (high velocity oxygenated fuel) thermal sprays	Hardness and wear resistance similar to hex chrome; limited to line-of-sight applications.	Sulzer Metco Western Hard Chrome
	Physical vapor deposition (PVD) -titanium nitride	Greater hardness than hex chrome with a thinner coating; less corrosion resistance	
	Ion beam-assisted PVD	Line-of-sight; thinner coatings give same properties as other thicker coatings	Skion Corp.
	Plasma spray -titanium carbide	Aluminum, steel, carbon steel, titanium substrates	A-Flame Corp.
	Chemical vapor deposition	Vacuum deposition; not limited to line-of-sight; resistant to acids; high deposition rate	
	Ion implantation	Ions are implanted – no thickness; non-line-of-sight	Southwest Research Institute
	Powder coating	Vacuum metallization (PVD) – has met OEM wheel industry testing requirements including ASTM B117, GM4472P, GM9508P, GM9682P, and GM6	PermaStar tm -Goodrich Technology Corp.
	Laser cladding	Non-line-of-sight; nickel carbide coating	Surface Treatment Technologies

Trivalent Chromium Plating Technology

In some applications and at certain thicknesses, trivalent chromium plating can replace hexavalent chromium. This is especially true for decorative applications where the trivalent chromium finish can closely resemble the hexavalent chromium finish. Generally, the trivalent chromium process is similar to that for hexavalent chromium except for the bath and the anode composition and/or configuration used. Trivalent chromium plating baths can be divided into the following three basic types:

1. Single electrolyte bath (chloride- or sulfate-based) using graphite or composite anodes and additives to prevent oxidation of trivalent chromium at the anodes.
2. Sulfate-based bath using shielded anodes (lead anodes surrounded by boxes filled with sulfuric acid) which prevent the trivalent chromium from reaching the anodes, thus preventing their oxidation.
3. Sulfate-based using insoluble catalytic anode that maintains an electrode potential level that prevents oxidation of the trivalent chromium.

Trivalent chromium baths overcome the shortcomings of hexavalent chromium in three general areas:

- Higher cathode efficiency
- Better throwing power
- Lower toxicity

Generally, the trivalent chromium plating rate and hardness of the deposit is similar to hexavalent chromium plating. Trivalent chromium baths also operate in the same temperature ranges as hexavalent chromium baths. Generally, the range of plating thickness for trivalent chromium is 0.005 to 0.050 mils. Trivalent chromium baths tend to be more sensitive to metallic impurities than hexavalent chromium baths. Impurities can be removed by using ion exchange or precipitating agents followed by filtration.

When trivalent chromium plating was first introduced, decorative customers generally did not accept the different color tones compared to hexavalent chromium. However, additives to the trivalent chromium bath can often adjust the tone to customers' decorative coating needs.

To more closely resemble the functionality of hard chromium plating, pulse current plating has been used in a trivalent chromium solution. However, these thicker trivalent chromium finishes have not quite matched the corrosion resistance of a functional hexavalent chromium finish.

Pollution Prevention for Trivalent Chromium Baths

While the use of a trivalent chromium process instead of a hexavalent chromium process is more protective of human health and the environment in and of itself, the potential pollution resulting from the trivalent chromium processes can be further reduced by using pollution prevention techniques. For example, static rinse tanks can be used to capture the drag out for return to the plating tank for reuse in the bath makeup water. In addition, the plating bath can be recycled and recovered for reuse using porous pots, membrane electrolysis, or ion exchange.

Current Research on Trivalent Chromium Baths

Concurrent Technologies Corporation (www.ctc.com) is currently testing functional trivalent chromium coatings from a few vendors. The results of this work should be available in 2004; contact technical manager Margo Neidbalson (NeidbalM@ctcgsc.org) for additional information.

Research is on-going in the area of charge modulated electrodeposition to enhance the plating of trivalent chromium by eliminating the adverse effects of hydrogen in the bath. (See Faraday Technologies in the Vendor section).

Benefits and Challenges

The trivalent chromium products share these benefits and challenges for potential users when compared to hexavalent chromium plating.

Benefits

Air Emissions

The trivalent chromium processes have higher cathode efficiencies than hexavalent chromium plating which results in less chromium mist emitted into the air. Therefore, air pollution treatment requirements are significantly reduced. Because air treatment is typically by wet scrubbing, wastewater treatment requirements are also significantly reduced.

Wastewater Treatment and Hazardous Waste Generation

The trivalent chemistries have a lower concentration of chromium in the bath, generally, 2/3 to 1 ounce/gal (5-7.5 g/L) of trivalent chromium compared to 17-30 ounces/gal (130-225 g/L) for hexavalent chromium. Therefore, there is much less chromium in each of the wastewater streams that needs to be controlled. The reduction step in wastewater treatment is not required (eliminating the use of sodium bisulfate or other reducing agents and additional acid for pH control) and therefore, significantly less sludge (by volume) is produced.

In addition, with trivalent chromium the anodes do not decompose, eliminating the sludge associated with hexavalent chromium anode decomposition. The trivalent chromium processes produce approximately thirty times less sludge (by volume) than the use of hexavalent chromium baths which can significantly reduce hazardous material handling and disposal costs. In addition, the chromium in the wastes is not in the more hazardous hexavalent form.

Energy Use

The trivalent chromium processes require less current density, so less energy is used compared with the hexavalent chromium processes.

Product Quality

The throwing power is better in the trivalent chromium processes. The trivalent chromium processes can also withstand current interruption without sacrificing finish quality, whereas the hexavalent

chromium processes cannot. Therefore, a trivalent process has the potential to lower touchup and rework costs, and improve customer satisfaction.

Production Rate

Due to the improved throwing power, rack densities can often be increased significantly.

Lower Toxicity

The trivalent processes are inherently less toxic due to the oxidation state of the chromium. In addition, the trivalent chemistries also require a lower concentration of chromium in the bath, generally, 2/3 to 1 ounce/gal (5-7.5 g/L) of trivalent chromium compared to 17-30 ounces/gal (130-225 g/L) for hexavalent chromium. Therefore, the toxicity of the trivalent chromium plating solutions is much lower than hexavalent chromium solutions.

Worker Exposure

The lower toxicity of trivalent chromium combined with the lower concentration of chromium in the bath and the substantial reduction in hazardous waste sludge produced mean that less hazardous material has to be handled. In addition, substantially less air emissions are generated from the trivalent chromium process. Finally, trivalent chromium baths have a higher pH than hexavalent baths, reducing the potential for adverse damage. Therefore, the use of trivalent chromium solutions provides less potential for worker exposure.

Regulatory Compliance

It is becoming increasingly difficult to comply with air emissions and worker health requirements of hexavalent chromium plating operations. Due to its lower toxicity, trivalent chromium is not regulated as aggressively, and therefore, compliance costs such as monitoring and recordkeeping can be lower.

Challenges

Chromium

Trivalent chromium processes still contain chromium, and therefore, are still potentially hazardous and could be subject to future increased regulation.

Cost

The actual cost of the trivalent and hexavalent chromium processes are dependant on many factors and are difficult to compare in a general sense. In general, chemical costs for trivalent chromium plating are more costly than hexavalent chromium plating. However, when increased production rates, and the costs of hazardous waste sludge disposal, and compliance with the restrictions placed on the use of hexavalent chromium by the EPA and OSHA are factored in, the use of trivalent chromium may be a good option for some applications. In addition, as noted previously, in some instances product quality can be improved, reducing rework costs.

Technical Capabilities

The trivalent chromium process may require more careful control than the hexavalent chromium process.

As mentioned previously, trivalent chromium baths tend to be more sensitive to metallic impurities. In addition, trivalent chromium plating may not be suitable to replace every hexavalent chromium plating requirement. For example, barrel plating with trivalent chromium solutions is possible, but difficult. Process conditions, part configuration and other variables must be controlled for successful barrel plating.

Change

Hexavalent chromium plating has been an industry standard for many, many years. Customers have been satisfied with its range of properties and cost and therefore demand it. Specifications often require hexavalent chromium plating. Platers are used to running hexavalent chrome baths. Change can be difficult for people to seek out and/or accept.

Foss Plating Case Study

(from the California Department of Toxic Substance Control, *"Replacing Hexavalent Chromium Plating with Trivalent,"* City Square, CA: California Department of Toxic Substance Control, 1995.)

Foss Plating in Sante Fe Springs, California, is a small, family-run chrome plating shop that has been in business more than 40 years. They converted a hexavalent chromium plating line to a fully automated single chrome-cell (III) system in 1989. At that time, the cost of conversion was approximately \$30,000.

As a result of the conversion, Foss Plating realized a return on their investment within the first year of operating the chrome (III) system. They saw an increase in productivity, greater system efficiency, fewer rejects, and lower treatment costs. The better throwing power and covering power of chrome (III) allowed them to increase the surface area on the racks by 70 percent. At the same time, they experienced a more than 90 percent decrease in the number of rejected parts and eliminated almost all need for color buffing. Foss also found that chrome (III) plated more efficiently from an energy standpoint.

The two biggest disadvantages Foss Plating experienced with chrome (III) were discoloration from impurities in the bath and the need to passify the non-plated areas of the parts.

Contacts for More Information

Vendors of Trivalent Chromium Chemicals

Mention of any company, process, or product name should not be considered an endorsement by NEWMOA, NEWMOA member states, or U.S. EPA.

MacDermid Incorporated (www.macdermid.com)

Francis DiGiovanni, fdigiova@MacDermid.com, phone: 203-575-5700

produces TriMAC Envirochrome. TriMAC Envirochrome contains boric acid; the system uses insoluble iridium oxide anodes. According to the manufacturer, “the system requires less DC power, produces no misting, and provides good throwing power.” TriMAC Envirochrome has a hardness of 1300 HV.

Atotech (www.atotechusa.com)

produces TriChrome® Plus, a decorative trivalent chromium process. Atotech states that the bath has a low chromium metal content, exceptional covering power and produces a micro-discontinuous deposit. This process is most appropriate for rack plating needs.

Enthone OMI (www.enthone-omi.com)

Linda Wing, lwing@cooksonelectronics.com, phone 248-740-7607

produces Tricolyte III, a trivalent plating process for use over bright nickel or nickel-iron deposits. Tricolyte III contains hydrochloric acid and ammonium hydroxide. The process uses graphite anodes with copper cores or titanium hooks. Enthone states that the product “will finish 50-1000% more parts per rack” than hex-chrome baths. Tricolyte III is said to have “excellent quality because whitewash, burning and other rejects due to poor coverage are eliminated.”

Liquid Development Company (www.ldcbrushplate.com)

offers LDC 2403-HTC³, a trichrome solution to replace hard chrome in brush plating applications. LDC 2403-HTC³ deposits have a hardness of 900-1200HV and can produce a deposit thicker than .0005 inches (0.125 mils).

Faraday Technologies (www.faradaytechnology.com)

Phillip Miller, miller.faraday@erinet.com, phone: 937-836-7749

In partnership with Atotech, Faraday Technologies has developed an approach to chemistry and waveform modification to enable functional chromium deposition from a trivalent bath. The electrically-mediated chromium plating process uses a fairly simple trivalent chromium electrolyte to deposit a chromium coating that is comparable to hexavalent chromium in thickness, hardness and rate. The recently completed Phase II project has established that chromium deposits up to 10 mil are feasible from this process. While the rate required for quality deposition of thicker coatings is slower than that for thinner coatings (<3 mil), the rate is similar to the rate for hexavalent chromium deposition.

Typically hexavalent chromium plating is performed using cathodic DC current. In this case, the waveform is modified to include cathodic DC current, anodic DC current and relaxation, or zero current, phases. The modulation of these current phases, including frequency and peak amperages, allow:

- improvements in mass transfer of chromium ions to the part surface, improving plating rate; and,
- reduction in hydrogen evolution at the surface, reducing hydrogen embrittlement and improving deposit characteristics such as corrosion resistance, adhesion, lower porosity, deposit stress.

State Technical Assistance Programs

In Connecticut: Kim Trella Department of Environmental Protection 79 Elm Street Hartford, CT 06106 (860) 424-3242	In Maine: Peter Cooke Department of Environmental Protection 17 State House Station Augusta, ME 04333 (207) 287-6188
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In Vermont: Greg Lutchko Department of Environmental Conservation 103 South Main Street Waterbury, VT 05671 (802) 241-3627	At NEWMOA: Jennifer Griffith NEWMOA 129 Portland Street, 6 th Floor Boston, MA 02114 (617) 367-8558, ext. 303

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The Northeast Waste Management Officials' Association (NEMWOA) is a nonprofit, nonpartisan interstates organization that addresses regional waste and pollution prevention issues. The membership is composed of state environmental agency directors of the hazardous waste, solid waste, waste site cleanup, pollution prevention and underground storage tank programs in Connecticut, Maine, Massachusetts, New Hampshire, New Jersey, New York, Rhode Island, and Vermont. NEWMOA provides a forum for increased communication and cooperation among the member states, a vehicle for the development of unified position on various issues and programs, and a source for research and training.