Executive Summary

Five Chemical Alternatives Assessment Study

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Overview

In July 2005, the Commonwealth of Massachusetts requested that the Toxics Use Reduction Institute perform an alternatives assessment for five chemicals: lead, formaldehyde, perchloroethylene (PCE), hexavalent chromium, and di(2-ethylhexyl) phthalate (DEHP). For each chemical, the Institute was charged with identifying significant uses in manufacturing, consumer products, and other applications; reviewing health and environmental effects; and evaluating possible alternatives. The Institute was also directed to evaluate possible effects on Massachusetts employment and economic competitiveness associated with adoption of alternatives. The study was conducted within a single fiscal year, and had a total budget of $250,000.

Rather than attempt to study all uses of each chemical, the Institute selected priority categories of use for each chemical. Likewise, for each use studied, the Institute chose a subset of possible alternatives for analysis. The Institute analyzed a total of sixteen different use categories and approximately one hundred different alternatives.

This report presents factual information on each alternative. The study does not provide a ranking of the alternatives; rather, it provides information that will allow users to make informed decisions and, in some cases, to design additional research to fill remaining information gaps. An important aspect of this alternatives assessment is its transparency: all information collected by the Institute is available for users to assess in the context of their specific applications, concerns and needs. Where the Institute was not able to obtain full information for a given parameter, this is clearly noted.

The results of this study will serve as a guide for those seeking safer substitutes to the five chemicals discussed here. In every case, at least one alternative was identified that was commercially available, was likely to meet the technical requirements of many users, and was likely to have reduced environmental and occupational health and safety impacts compared with the base chemical. In addition, the methodologies piloted in this study should prove useful as a model for future efforts at alternatives assessment. Alternatives assessment is a relatively new and highly promising methodology for analyzing products and processes that affect human health or the environment. The present study helps to demonstrate the viability of alternatives assessment as a useful tool to support decision-making about chemicals and their alternatives.

Approach and Methodology

During the year, five teams of Institute staff and outside experts performed parallel alternatives assessments using a common process and methodology. The project was divided into three phases. In the first phase, the Institute identified uses of the five chemicals within Massachusetts, and prioritized a subset of those uses to analyze in depth. In the second phase, the Institute identified alternatives and, again, chose priority alternatives for further study. In the third phase, the Institute conducted detailed research on each of the priority alternatives, gathering information on the health and environmental, technical, and economic aspects of each alternative. For each phase of the analysis, the Institute relied on information from experts and publicly available resources. The Institute also consulted extensively with stakeholders, including industry representatives, government agencies, and public health, environmental and labor advocates.

Prioritization of Chemical Uses

Each of the five chemicals considered in this study has a wide range of uses. The Institute selected a subset of these uses based on the importance of each use in Massachusetts, the potential availability of alternatives, the extent of possible exposures for workers and the general population, and the potential utility for Massachusetts businesses and citizens of the alternatives assessment. To maximize the value of this pilot project, the Institute also made an effort to include a mix of uses relevant for industry, small business, and consumer products. The Institute placed a low priority on uses where alternatives are already being readily adopted, or where significant research on alternatives is being carried out by others.

For hexavalent chromium and DEHP, the uses selected for this study represent a large percentage of total use of these chemicals in Massachusetts manufacturing. Lead and formaldehyde, on the other hand, have a multitude of uses beyond those examined here. For perchloroethylene, the study incorporated uses of particular relevance for small businesses and consumer exposures. The assessments conducted for this study can be used as a model for future assessments of other uses.

Prioritization of Alternatives

Alternatives to toxic chemicals may include drop-in chemical substitutes, material substitutes, changes to manufacturing operations, changes to component/product design, and other technological or market solutions. The Institute identified more than 200 possible alternatives for the chemical uses of interest, then applied a health and environmental screen to all alternatives. The screen excluded any chemical that was a known or probable human carcinogen, failed a persistence, bioaccumulation, and toxicity (PBT) screen, or was included on the 1999 More Hazardous Chemicals list developed by the Massachusetts Toxics Use Reduction program's Science Advisory Board. Of the options that passed this initial screening, the Institute prioritized alternatives for further study based on additional information about viability, health and environmental effects, economic considerations, and importance to stakeholders. The Institute also chose to prioritize products or materials manufactured in Massachusetts. When several alternative chemicals or materials could be grouped together, the Institute selected a representative of that grouping for detailed consideration.

The individual chapters provide detailed information on the process by which the Institute chose the list of alternatives to assess for each chemical use. It is important to note that inclusion of an alternative in the assessment does not imply an endorsement of that alternative. Similarly, exclusion of an alternative from the assessment does not imply that it has been rejected. In some cases, alternatives have been excluded from this assessment simply because they have been studied in depth in another context.

Some alternatives, particularly those comprised of single chemicals, were assessed as generic alternatives. Other alternatives vary considerably depending on the precise formulation or manufacturer. In these cases the Institute assessed a representative product. The choice of a particular manufacturer's product as representative does not constitute an endorsement of that product, or indicate that other similar products are not worthy of consideration.

Alternatives Assessment

The alternatives assessment included consideration of health and environmental effects, technical feasibility, and financial feasibility.

- **Health and environmental effects.** The Institute evaluated a subset of environment, health and safety (EH&S) endpoints. The Institute did not perform a detailed toxicological review for each alternative. Rather, the study relied on information obtained from authoritative bodies, emphasizing the most recent validated data or data that has been referenced by a US government agency. Where this type of information was not available, or where more recent studies called into question the results previously published by authoritative bodies, supplementary information was noted. The Institute relied on the U.S. EPA PBT Profiler software to gain information on persistence, bioaccumulation potential and toxicity. In cases in which it was necessary to evaluate chemicals in mixtures, the assessment considered each of the chemical constituents, excluding those making up 1% or less by mass of the mixture.

- **Technical feasibility.** The study identified and assessed application-specific performance requirements that must be met for each feasible alternative. The performance information that the Institute was able to obtain varied considerably among uses. For some uses information was obtained from published studies or directly from technical experts or several users of the alternatives. For other uses the Institute relied on information provided by product manufacturers. The type of performance information that was available for a given alternative will affect the degree and nature of follow-up that may be necessary for users to draw conclusions about technical feasibility for individual applications.

- **Financial feasibility.** Data sources for financial information included manufacturers, stakeholders, the Chemical Economics Handbook and other standard reference sources. In many cases, particularly for emerging alternatives, no hard cost information was available. In other cases, sufficient cost information exists to conclude that the alternative is either more or less costly than the current chemical use. The Institute recognizes that cost comparisons today may be of limited relevance for emerging technologies and technologies that are gaining in popularity, since learning curves, economies of scale, and other factors can reduce costs over time.

It is important to note that this study was not designed to assess the relative safety of one alternative over the other. Rather, alternatives were compared to the study chemical as a baseline. This report provides information in the three assessment areas for each alternative and invites readers to use and supplement this material as appropriate for the specific considerations and requirements that they face. Users should use the material presented here for guidance in conducting their own assessments, taking into account the values, priorities, and situation-specific requirements that are most relevant for their organizational, industrial, or policy goals.

Economic Impact Assessment

In addition to collecting financial information as part of each alternatives assessment, the Institute convened a group of economists and other experts to discuss broader economic patterns, including the possible impacts on employment and competitiveness from adopting alternatives in Massachusetts.

Lead and Lead Compounds

Lead is a naturally occurring metal with a high density and low melting point. It is ubiquitous in manufactured products in many forms: as a pure metal, as an alloy with other metals, and in compounds. It is valued for its electrical conductivity, high density, and ability to stabilize plastics.

Lead poses a serious threat to human health and the environment. Acute human health effects of high lead exposures can include gastrointestinal distress, brain and kidney damage, and death. Chronic effects of lead exposure include anemia, damage to the nervous system, effects on blood pressure and kidney function, and interference with vitamin D metabolism. The U.S. Environmental Protection Agency (EPA) has classified lead as a probable human carcinogen, and the International Agency for Research on Cancer (IARC) has classified inorganic lead as probably carcinogenic to humans (Group 2A). Fetuses, infants and children are particularly vulnerable to adverse effects from lead exposure, including irreversible neurological damage. There is no known safe threshold for lead exposure in children.

Lead is extremely persistent in both water and soil. Combustion of leaded gasoline was a major source of anthropogenic lead releases in the past. Industrial releases from smelters, battery plants, chemical plants, and disturbance of older structures containing lead based paints are now major contributors to total lead releases.

The Institute selected three priority uses of lead to assess in detail: ammunition, weighting applications, and heat stabilizers for PVC wire and cable coatings. These applications were chosen based on stakeholder interest, importance to Massachusetts industry and consumers, and likely availability of alternatives. Ammunition used at indoor and outdoor firing ranges is a significant source of occupational lead exposure and environmental contamination. Automotive wheel weights and fishing sinkers were chosen as representative of a large number of lead uses that rely on its high density. Wire and cable heat stabilization is the category with the largest use of lead among Massachusetts manufacturers. The results of these assessments are summarized below.

Ammunition for shooting ranges

Most practice shooting ranges currently use lead ammunition. Range operators and shooters can be exposed to high airborne lead levels in indoor shooting ranges. Use of lead ammunition at outdoor shooting ranges can produce environmental contamination.

Most of the major ammunition manufacturers now market lead-free bullets. A few smaller ammunition manufacturers specialize in the production of lead-free ammunition.

The Institute examined five possible alternatives to lead ammunition for use in shooting ranges: bismuth, copper, iron, tungsten, and zinc. For each alternative, the Institute examined human health, environmental, technical, and cost criteria.

- **Human health.** The alternative materials are all superior to lead from a human health perspective for the criteria the Institute considered (carcinogenicity, developmental toxicity, and occupational exposure).
- **Environment.** In general, the alternatives are more desirable from an environmental standpoint, with the exception of aquatic toxicity for copper and zinc.
- **Technical criteria.** Technical criteria of interest for this application include density, frangibility, and barrel wear.
    - Greater bullet density is advantageous for most ammunition applications, since high bullet weight and small bullet size are both desired characteristics. Tungsten has greater density than lead, while the other alternatives have lower density than lead. However, the density of bismuth is very close to that of lead. One manufacturer produces bismuth bullets that match the weight of many lead bullets.
    - Many lead-free bullets are frangible, which means they fragment into small particles upon impact with a target. Frangible bullets are safer than lead bullets for use at indoor firing ranges because they reduce or eliminate the dangers associated with ricocheting bullet fragments. This is of particular concern when firing at steel targets at close range. Frangible bullets can also limit damage to steel targets. Bismuth, iron, tungsten/nylon, and powdered copper can all be used to make frangible bullets. Solid copper bullets are not frangible and may ricochet more readily than lead bullets. Some zinc bullets break apart upon entering a target, but their probability of ricochet is not known.
    - Barrel wear is the erosion of barrel material by bullets. All of the alternative materials except tungsten are similar to lead from the perspective of barrel wear.
- **Cost.** All the alternatives currently have a higher purchase price than lead bullets. However, all the alternatives are superior to lead bullets from the perspective of operating costs. Firing ranges face numerous costs associated with the use of lead ammunition. These can include costs of air monitoring, blood lead level testing of range operators, maintenance of containment and filtration systems, purchase of replacement filters, range cleaning, and lead

disposal. By switching to lead-free ammunition, firing ranges can reduce or eliminate costs in these areas. In addition, lead bullets and bullet fragments must be either recycled or disposed of as hazardous waste. Alternative bullets, in contrast, can be disposed of as non-hazardous waste if they are not recycled. Frangible bullets also reduce wear and damage on bullet traps and backstops.

Weighting applications

The Institute chose wheel weights and fishing tackle as two examples of the larger category of lead used in weighting applications.

Fishing sinkers

Nearly 2,500 metric tons of lead are used each year in the United States to produce fishing sinkers. Many of these sinkers are lost during use. One study found that anglers lost, on average, one sinker every six hours of fishing.

Lead sinkers are lethal to waterbirds, such as loons and swans. One study found that the most common cause of death in adult breeding loons was lead toxicity from ingested fishing sinkers.

A number of states have placed limits on the use of lead fishing sinkers. In Massachusetts, lead sinkers are prohibited for use in the Quabbin and Wachusett Reservoirs, the two bodies of water that support the core of the state's loon population. Use of lead sinkers is restricted in several other states in the Northeast, and is restricted or banned in several countries.

Many anglers produce their own lead sinkers at home. This activity can expose individuals and family members to airborne lead particles or vapors.

The Institute examined five possible alternatives to lead for use in fishing sinkers: bismuth, ceramic, steel, tin, and tungsten. For each alternative, the Institute examined human health, environmental, technical/performance, and cost criteria.

- **Human health.** All the alternative materials are superior to lead from the perspective of the human health criteria the Institute examined (carcinogenicity, developmental toxicity, and occupational exposure).
- **Environment.** The alternatives are generally superior to lead from an environmental standpoint as well. All of the alternatives are clearly less hazardous to waterfowl and other aquatic species than lead.
- **Technical criteria.** The principal technical criteria of interest for this application are density, hardness, malleability, melting point, and corrosion resistance.
  - Tungsten is more dense than lead; all the other alternatives are less dense than lead.
  - Harder materials are preferable for use in many sinkers. All the alternatives are harder than lead; pure tin is about equal to lead in hardness, while tin alloy is harder than lead.
  - Greater malleability is an advantage for sinker applications where the sinker is crimped on to the fishing line. Tin has malleability equal to that of lead; all of the other alternatives are less malleable than lead.
  - Low melting point is considered an advantage because it allows individuals to produce sinkers at home, although home production of lead sinkers also creates

human health hazards. Bismuth and tin have lower melting points than lead; ceramic, steel, and tungsten have higher melting points.

    - Carbon steel is less resistant to corrosion than lead. Stainless steel and all the other alternatives are similar to lead in this regard.

- **Cost.** The alternatives generally have a higher retail price than lead sinkers, although some steel sinkers are competitive in price with lead sinkers. Studies conducted in the 1990s suggested that fishing sinker purchases represent less than 1% of total expenditures by anglers on their sport, so an increase in fishing sinker costs would be unlikely to have a significant effect on users.

Wheel weights

Wheel weights often fall off automobile wheels, leading to lead contamination of the environment. Worker exposure is a concern in the installation of wheel weights.

There is a thriving market in lead-free wheel weights. European and Japanese automobile manufacturers have already switched to lead-free wheel weights and U.S. automobile manufacturers are currently in the process of making the switch. Asian auto manufacturers now primarily use steel weights. Zinc weights are used widely in Europe, and US auto manufacturers are using zinc weights for automobiles destined for export to Europe. General Motors and Ford are in the process of converting to steel weights.

Despite these developments, the U.S. market in replacement wheel weights continues to use lead weights almost exclusively. This market in replacement weights accounts for 80% of total wheel weight use in the U.S.

The Institute examined four possible alternatives to lead wheel weights: copper, steel, tin, and zinc. For each alternative, the Institute examined human health, environmental, technical/performance, and cost criteria.

- **Human health.** All of the alternative materials are superior to lead for the human health criteria the Institute examined (carcinogenicity, developmental toxicity, and occupational exposure).

- **Environment.** For the most part the alternatives are superior environmentally, although zinc is inferior for aquatic toxicity in salt water, and copper is inferior for aquatic toxicity in both fresh and salt water.

- **Technical criteria.** The principal technical criteria of interest for this application are density, malleability, and corrosion resistance.

    - All of the materials considered in this analysis are less dense than lead. Thus, in order to achieve the same mass, the weights made from alternative materials must be somewhat larger than their lead counterparts. This adjustment does not typically pose engineering difficulties for weights used on passenger vehicles.

    - The malleability of lead makes it possible to shape wheel weights to match the curve of the wheel diameter. The malleability of copper and tin is similar to that of lead; steel and zinc are less malleable. Manufacturers can compensate for lower malleability by creating segmented weights.

  - The corrosion resistance of the alternative materials is generally similar to that of lead; tin is superior to lead in this regard because it does not require coating.

- **Cost.** Copper and tin weights are expected to cost more than lead weights at initial purchase; zinc weights cost about the same as lead weights, and steel weights have equal or lower cost. The end of life costs for all the alternatives are lower than those for lead.

Heat stabilizers for PVC wire and cable coatings

Lead heat stabilizers used for polyvinyl chloride (PVC) constitute the largest use of lead compounds in Massachusetts manufacturing, and the wire and cable industry is the largest user of these compounded resins.

Significant progress has been made in the identification and adoption of alternatives. Many lead-free heat stabilizers are commercially available, and resin compounders are working proactively with wire and cable companies to encourage their adoption. Regulatory requirements prohibiting the use of lead and other hazardous substances in electrical and electronic equipment in the European Union have created an incentive for U.S. manufacturers to develop lead-free alternatives. The Institute is engaged in on-going collaborative projects to help Massachusetts industries to gain and maintain a competitive edge in producing lead-free wire and cable, as well as lead-free electrical and electronic equipment.

The Institute did not conduct a complete technical assessment for alternative heat stabilizers. Each application has unique technical requirements, and stabilizers are formulated with many different combinations of chemicals to suit each application. Furthermore, heat stabilizers will be examined as part of a collaborative project between the Institute and the U.S. EPA to conduct a detailed life cycle assessment for three specific wire and cable applications. However, many Massachusetts wire and cable companies plan to adopt lead-free alternatives before that study will be complete. Thus, stakeholders determined that it would be useful for the Institute to analyze the environmental health and safety profiles of chemicals that are widely used in alternative stabilizers.

The Institute gathered information on five categories of alternative heat stabilizers: calcium-zinc, barium-zinc, magnesium-zinc, magnesium aluminum hydroxide carbonate hydrate, and magnesium zinc aluminum hydroxide carbonate. From these categories, the Institute selected five representative heat stabilizer products and conducted an environmental health and safety assessment of their constituent materials. Many of these constituent materials were found to be superior to lead from a human health and environmental perspective. Costs of mixed metal heat stabilizers have decreased in recent years, such that a transition to a mixed metal heat stabilizer may be cost neutral. Where a cost differential exists, it is estimated at 10% or less.

Formaldehyde

Formaldehyde is a naturally occurring chemical found in small quantities in the human body. Products that are made from or contain formaldehyde include many resins, permanent press fabric treatments, lawn fertilizers, cosmetics and disinfectants. Wood adhesives used to make plywood, particleboard and other manufactured wood products are the dominant end use for this chemical. The plastics industry also uses formaldehyde-based resins extensively. Formaldehyde is also used as a sterilant and tissue preservative. It is used to preserve animal specimens used in secondary school and college biology classes. It is also used to preserve human and animal tissue in medical and scientific laboratory settings. Embalmers use formaldehyde to preserve human remains for burial.

Formaldehyde exposure through consumer products or industrial activity is very hazardous to human health. Formaldehyde is highly irritating, acts as a potent sensitizer, and is known to cause cancer in humans. In 2004 IARC moved formaldehyde from Group 2A (probable human carcinogen) to Group 1 (known human carcinogen). Ingestion of formaldehyde or exposure to very high air concentrations can cause death.

The Institute assessed alternatives to formaldehyde in three categories of use: sanitary storage in barbering and cosmetology, preserved educational specimens for dissection, and building panels.

Sanitary storage in barbering and cosmetology

The Massachusetts Board of Cosmetology requires cosmetology salons to use dry sanitizer made from paraformaldehyde (a polymerized solid form of formaldehyde) in drawers where instruments are stored. The perforated plastic containers containing para-formaldehyde emit formaldehyde as it de-polymerizes into formaldehyde gas, filling the cabinets and drawers where hair brushes are kept, and subsequently entering the salon and classroom air as drawers are opened. Use of this dry sanitizer has placed a consistent source of formaldehyde in salons and cosmetology training schools, including vocational high schools.

The Institute identified and evaluated two possible alternatives to the use of dry sanitizer in drawers. The first option is a process change: storage of implements in a disinfected, dry, covered container or drawer without the use of any additional sterilant. The second option is to use ultraviolet (UV) light cabinets for sanitary storage.

The Massachusetts Board of Cosmetology is the only such board in the U.S. that requires use of dry sterilants. In contrast, the National-Interstate Council of State Boards of Cosmetology (NIC) does not recommend use of formaldehyde-based dry sterilants due to their carcinogenic potential. In place of dry sterilants, the NIC recommends an alternative procedure of proper cleaning, wet disinfection, drying and storage. The disinfection and storage practices recommended by the NIC are reiterated in the rules of many other Boards of Cosmetology and in the field's primary textbook and practice guidance.

Process change

One practical alternative to use of dry sterilant is simply to store implements in a disinfected, dry, covered container that is isolated from contaminants. This option would produce cost savings, because it would eliminate the need for cosmetology salons to purchase dry sterilant.

Simple elimination of dry sterilant, without any other change in procedures, is superior to use of dry sterilant from the human health, environmental, and cost perspectives. It is equivalent from a technical perspective.

UV light cabinets

Another option is for cosmetology salons to use UV light cabinets. A disadvantage of this technology is that although UV germicidal light is effective at killing pathogens, it must strike all surfaces and this is difficult to achieve on a brush. The cabinets may also become reservoirs of pathogens if they are not regularly cleaned and disinfected.

Use of UV storage cabinets is superior to use of dry sterilant from a human health and environmental perspective, although there is the potential for UV light exposure if the cabinets are misused. This system has a higher cost than dry sterilant.

Preserved educational specimens for dissection

Secondary school and college students in anatomy classes dissect preserved specimens, including fetal pigs, frogs, cats, sharks and other species. Traditionally, educational specimens have been preserved with a formalin solution (a 37% solution of formaldehyde in water). Formaldehyde kills the bacteria that would otherwise decay the tissue. It also polymerizes the tissue, helping to maintain its texture, structure and color. This application does not account for a large percentage of formaldehyde use, but it poses particular public exposure concerns. Students, laboratory instructors and technicians are exposed to formaldehyde through their repeated contact with these specimens.

The Institute evaluated two categories of alternatives: use of specimens that are formaldehyde-free, and the technological alternative of video and virtual dissection.

Specimens in alternative solution

Using specimens of grass frogs as a typical application, an outside expert evaluated the technical performance of three alternative preservatives: Formalternate by Flinn Scientific, Wardsafe by Ward Scientific, and Streck Tissue Fixative (S.T.F.) Preservative by Nebraska Scientific. Formalternate is a combination of propylene glycol, ethylene glycol phenyl ether and phenol. Wardsafe is primarily glutaraldehyde. S.T.F. is a mixture of diazolidinyl urea, 2-bromo-2-nitropropane-1, 3-diol (Bronopol), zinc sulfate, and sodium citrate. Different species may be preserved in different solutions by the same company. All these alternative products are readily available from well-established companies.

- **Health.** All three alternatives are superior to formaldehyde-containing specimens from the perspective of carcinogenicity, sensitizing potential, and capacity to cause irritation. Some ingredients of the alternatives can cause skin, eye and respiratory irritation, and some can act as sensitizers, but they are less hazardous than formaldehyde on all these measures. Evaluating the health effects of Formalternate and S.T.F. is complicated by the fact that they are chemical mixtures. Glutaraldehyde, used in Wardsafe, has high acute toxicity, but is present at low concentrations in the specimen.

- **Environment.** Some of the chemicals used in the alternative fixatives are more toxic to fish and other species than is formaldehyde. In general, the low volatility and small amounts of preservative in the alternative specimens suggests that exposure for humans and the environment are likely to be very low. Life cycle considerations for the alternatives include the use and disposal of some ingredients, such as phenol and zinc sulfate, which are potential environmental pollutants.

- **Technical criteria.** All of alternatives match or exceed the important technical and performance criteria for educational specimens: color, texture, and stiffness of the specimen tissue. The color of the alternative specimens was as good as or better than the formalin-preserved specimen. The specimens varied in texture but all had acceptable characteristics.

- **Cost.** The prices of alternative specimens are similar to each other and generally less expensive than the formalin-fixed specimen.

Process change: Video dissection

Another alternative is to use video/virtual dissection instead of physical dissection of a preserved specimen.

- **Health and Environment.** Video/virtual dissection does not pose any of the health or environmental hazards for students or instructors associated with dissection of preserved specimens.
- **Technical criteria.** Video/virtual dissection offers different pedagogic opportunities from those afforded by physical dissection. Some instructors believe that video dissection is not an adequate substitute for dissection of preserved specimens, although it may be a useful supplement. However, the educational utility of video and/or virtual dissection may vary with the class or instructor. A complete assessment of the educational benefits of each option was beyond the scope of this study.
- **Cost.** The cost of video/virtual dissection programs is variable. Low or no-cost materials are available, as are more expensive programs. In contrast to preserved specimens, these represent a one-time cost.

Hardwood plywood and structural use building panels

Adhesives used to make plywood, particleboard and other manufactured wood products account for the majority of formaldehyde consumed world wide each year. The components of wood panels vary depending on their intended use. Plywood and other products that are "exterior-grade" or need to withstand wet conditions are usually made with phenol-formaldehyde resin. Particleboard and medium density fiberboard, often used for making furniture and cabinetry, are made with less expensive urea-formaldehyde resins, which have higher levels of formaldehyde emissions. Melamine-formaldehyde resins and polyacetal resins are also used in wood products and laminates and in molded plastic parts.

The Institute examined three alternatives that are currently available: Columbia Forest Products soy-based resin hardwood plywood panels, Homasote's recycled paper panel boards, and Viroc's wood fiber Portland cement panels. The Institute also assessed one emerging alternative that is not yet on the market, JER EnviroTech's plastic-wood fiber panel.

Hardwood plywood

The Columbia Forest Products soy-based resin hardwood plywood panel (Purebond) is a hardwood veneer core plywood panel. It can be used to make cabinets, built-in furniture, paneling, shelving, doors and other uses requiring a high end wood product.

- **Human health.** Purebond is superior to formaldehyde-resin plywood from the perspective of carcinogenicity and irritation/sensitizing properties. It eliminates potential formaldehyde exposures for users. However, its production involves use of epichlorohydrin as an intermediate. Epichlorohydrin is classified as a probable human carcinogen and poses other hazards to human health and the environment. This chemical could be a hazard to workers and the environment during production.

- **Environment.** The formaldehyde-based resin in conventional plywood has minor ecotoxicity. Purebond is similar to formaldehyde-resin plywood for this parameter.
- **Technical Criteria.** Technical characteristics of interest for this application include appearance/construction, strength of the glue bond when moist, fire resistance, warp resistance, and product availability. Purebond is similar to formaldehyde-containing plywood for the parameters of appearance/construction, fire resistance, and product availability. It has a glue bond superior to that of urea-formaldehyde plywood under conditions of moisture. Its warp resistance has not been assessed fully.
- **Cost.** Purebond is currently available at a similar cost to formaldehyde-resin plywood.

Structural use panels

The Institute assessed two alternatives that could be used in place of softwood plywood for structural use panels: Homasote's recycled paper panel boards, and Viroc's wood fiber Portland cement panels.

Homasote's recycled paper panels and Viroc's wood fiber Portland cement panels may be used in place of softwood plywood and oriented strand board (OSB) in exterior sheathing, roof decking and floor decking. Viroc is used extensively in Europe.

- **Health.** Viroc and Homasote do not present a hazard to building occupants, but there are some occupational exposure concerns, such as exposure to wood and cement dust during cutting. Both products are superior to formaldehyde-resin plywood from the perspective of carcinogenicity of the binder. The Homasote panels are superior from the perspective of irritant in binder, while the Viroc panels are similar to formaldehyde-resin plywood on this metric.
- **Environment.** Both products are superior to formaldehyde-resin plywood from the perspective of ecotoxicity and natural resource conservation. The Viroc product is inferior from an energy intensity life cycle perspective.
- **Technical criteria.** Technical and performance criteria of interest for these uses include strength, weight, response to moisture, storage, handling, fastening, finishing, fire resistance, thermal resistance, and mold, rot and insect resistance. Both alternatives present some advantages and some disadvantages on these metrics. For example, Homasote is superior to formaldehyde-resin panels on several measures including resistance to insects, rot, and mold, and is inferior on certain other measures, such as impact resistance and tensile strength. Viroc is superior on measures including resistance to insects, rot, and mold, fire resistance, and impact resistance, and inferior on parameters such as tensile strength. Both Viroc and Homosote panels must be thicker and heavier than formaldehyde-resin panels to withstand an equivalent load over the same span.
- **Cost.** Both alternatives are currently more expensive than traditional formaldehyde-containing plywood.

Emerging alternative

The JER Envirotech Company is in the process of developing an extruded building panel made of wood fiber and polypropylene thermoplastic. This is an "emerging technology" that may substitute for particleboard and structural uses. The Institute did not assess this alternative in detail, but encourages further study of this option.

Perchloroethylene

Perchloroethylene (PCE) is a synthetic chlorinated hydrocarbon. It is used primarily as a solvent in dry cleaning and industrial degreasing and as a chemical intermediate.

Short-term exposure to PCE can cause symptoms such as skin, eye, and respiratory irritation, headache, and nausea; very high exposure can be fatal. Long term exposure to PCE may cause liver, kidney or central nervous system damage. PCE may also affect the developing fetus. IARC lists PCE as a probable human carcinogen (Group 2A).

PCE most often enters the environment through fugitive emissions from dry cleaning and metal degreasing industries and by spills or accidental releases to air, soil or water. Exposure results from environmental contamination, presence in consumer products or occupational sources. PCE has been found in breast milk, one indication of its ubiquitous presence in the environment.

The Institute assessed alternatives to PCE in three categories of use: dry cleaning, vapor degreasing, and aerosol automotive cleaning.

Dry cleaning

The Institute analyzed five categories of PCE alternatives for dry cleaning: hydrocarbons (HC), volatile methyl siloxanes (VMS), substituted aliphatic glycol ethers (SGE), wet cleaning, and liquid carbon dioxide (CO_2). Like PCE, the first three of these categories are based on organic solvents. For each category except CO_2, the Institute selected an individual chemical or process as a representative of the broader category.

- **Health.** All the alternatives are superior to PCE from the perspective of carcinogenicity. VMS and CO_2 are superior from the perspective of irritation, while SGE and wet cleaning are roughly equivalent to PCE on this metric. HC, wet cleaning, and CO_2 are superior from the perspective of exposure limits. Recent research has raised concerns about adverse effects of decamethylcyclopentasiloxane (D5), the dry cleaning solvent used in the VMS system, in laboratory animals.
- **Other hazards.** Unlike PCE, HC and VMS are combustible.
- **Environment.** The alternatives are less persistent than PCE in water, soil, sediment, and air, with some exceptions: the hydrocarbon alternative is more persistent than PCE in soil. The CO_2 used in the process is captured from industrial processes and thus the garment cleaning adds no net CO_2 to the atmosphere.
- **Technical criteria.** The first four alternatives are commercially available in Massachusetts. No commercial CO_2 facilities were identified in Massachusetts, although there are facilities in other states. Thus, all of the alternatives are known to have commercial viability at this time. Technical criteria of interest for this application include time for washing; load capacity; the range of soils that can be removed effectively; the types of clothing that can be washed using a given system; and the efficiency of spot cleaning before washing.

    - All the alternatives require more time for cleaning than PCE, except CO_2, which requires less time. This time differential is decreasing as operators gain more experience with the alternatives. The alternatives are variable on the metric of load capacity: VMS is superior on this metric and wet cleaning is superior in some cases, while carbon dioxide is similar to PCE and HC and SGE are inferior.
    - The hydrocarbon and VMS alternatives are able to clean fewer types of soil compared with PCE. The SGE and carbon dioxide systems are similar to PCE on this metric. Wet cleaning can be either equivalent or inferior to PCE on this metric.
    - HG and SGE are superior to PCE in the range of types of clothing that they can clean. VMS is similar to PCE on this metric, and wet cleaning and carbon dioxide are more limited in the range of clothing types they can clean.
    - Carbon dioxide is superior on the spotting metric; hydrocarbon, VMS and wet cleaning are inferior; and SGE can be either similar or inferior to PCE on this metric.

- **Cost.** Cleaning system costs include equipment, solvent, labor, energy, and regulatory costs. The Institute gathered comparative cost information on these parameters from a number of Massachusetts cleaners. Hydrocarbon systems have higher equipment and labor costs, counterbalanced by lower solvent and regulatory costs. VMS systems have higher equipment cost; figures were unavailable for several other parameters. SGE systems have higher equipment and solvent costs, counterbalanced by lower regulatory costs. Wet cleaning has higher labor costs, counterbalanced by lower equipment, solvent, and regulatory costs. Carbon dioxide has higher equipment costs and lower regulatory costs.

Vapor degreasing

The Institute carried out alternatives assessments on one product based on n-propyl bromide (nPB), a product based on a volatile methyl siloxane (VMS), and two hydrochlorofluorocarbons (HCFCs). All of these are solvent-based vapor degreasing substitutes for PCE. The Institute did not conduct an alternatives assessment on aqueous cleaning systems as part of this project because the Institute's Surface Solutions Laboratory has already produced extensive resources in this area. As documented in other work by the Institute, approaches other than use of a drop-in solvent replacement are often superior from a health, environmental, technical and cost perspective.

- **Health.** All of the alternatives have potentially significant environmental and occupational health and safety impacts. The HCFC products have significant adverse environmental impacts, including persistence and global warming potential, but should be somewhat less toxic than PCE. There are significant concerns about the toxicity of nPB; it is a neurotoxin, and its carcinogenicity is now under study. Exposure to high levels of VMSs can cause dizziness, disorientation, and shortness of breath.

- **Other hazards.** All of the alternatives have higher vapor pressures than PCE, which will lead to greater evaporation and the potential for more vapors to escape from the degreaser; this will increase the potential for worker exposure, and may cause greater fugitive emissions than with PCE. A significant safety hazard is presented by the VMS product, which is highly flammable with a very low flash point. Its use as a vapor degreaser would present a significant fire and explosion hazard, and special handling would be required to use it safely, including the requirement for a closed system, spark-proof equipment, and worker training.

- **Environment.** nPB and VMS are superior to PCE on measures of persistence in water, soil, sediment, and air. The two HFCs are inferior on these measures. nPB is superior from the perspective of bioaccumulation, while the others are inferior on this measure. The two HFCs also have global warming potential.
- **Technical criteria.** Over all, the vapor degreasing alternatives have technical features comparable to those of PCE. The alternatives all have higher vapor pressures than PCE, which will contribute to product loss through evaporation. On the other hand, the alternatives all have lower surface tensions than PCE, which should enhance their ability to clean complex parts. Soil removal testing performed at the Institute's Surface Solutions Laboratory found that all four alternatives were as effective as PCE in removing oil-based soils.
- **Cost.** All the alternatives currently cost more to purchase than PCE, creating an initial barrier for companies interested in switching to an alternative vapor degreaser. Operating costs such as energy use, waste solvent handling costs, and solvent lifetime may help to offset this higher purchase price. For example, many of the alternatives can be used at lower operating temperatures than PCE to achieve the same level of cleaning performance. On the other hand, all of the alternative solvents are more volatile than PCE, which might increase costs due to greater evaporative losses.

When addressing a specific cleaning need it is important to consider all options, including process and product modifications. Therefore, other options to consider include alternative cleaning processes such as an aqueous or a semi-aqueous system, working within the supply chain to change the contaminant on the part that requires cleaning, or investigating a material change to prevent contamination and thereby making cleaning unnecessary. All of these options would be preferable to using PCE or any of the drop-in alternatives discussed here. The Institute has demonstrated the viability of this approach in projects to assist industry in replacing chlorinated solvents with safer alternatives.

Aerosol automotive cleaning

The Institute carried out alternatives assessments on four brake cleaning alternatives, seven external engine cleaning alternatives, three internal engine cleaning alternatives, and four tire cleaning alternatives.

- **Health.** With regard to human toxicity, products containing n-hexane, 2-butoxyethanol, DGME, toluene, and glycol ethers are of equal or more concern compared with products containing PCE. Aqueous-based products will have lower human health concerns than any of the solvent-based products.
- **Other hazards.** Most of the solvent-based cleaners are highly flammable, and great care must be taken in their use, especially around hot engines. PCE is nonflammable, as are the aqueous-based cleaners, so these alternatives are preferable with regard to fire potential.
- **Environment.** Many of the alternative cleaners have the potential for significant environmental impact upon release. The medium of most concern is air, since these products are used as aerosol sprays. Most of the alternative products have ingredients with atmospheric half-lives exceeding two days and thus, like PCE, are considered persistent.

- **Technical criteria.** It is difficult to assess the technical performance of the alternatives objectively, since test data are not available. Stakeholders indicated that the alternative solvent-based cleaners are likely to perform as well as PCE-based cleaners, while aqueous-based cleaners may require more mechanical agitation to achieve equivalent results.
- **Cost.** Cost information is also difficult to assess. Some alternative products were more expensive per ounce than the corresponding PCE product, and some were less expensive per ounce. The actual cost per use may be quite different, however, since more or less of the different products may be required to obtain equivalent levels of cleaning.

Hexavalent Chromium

Chromium is a metallic element found in nature in the form of chromite ore or the mineral crocoite. Chromium provides manufactured products with hardness, shininess, durability, color, corrosion resistance, heat resistance, and decay resistance. Important uses of chromium compounds include wood preservation, metal processing, leather tanning, and production of pigments. The major application of chromium is in the production of alloys, primarily stainless steel; historically, this has amounted to 50-60% of total chromium use.

There are several oxidation states of chromium, each with its own chemical characteristics. The most common forms are trivalent chromium and hexavalent chromium. Trivalent chromium compounds occur naturally, while the hexavalent compounds result primarily from industrial activity.

Hexavalent chromium poses far more health hazards than trivalent chromium. Short-term effects of hexavalent chromium exposure can include eye and respiratory irritation and sensitization. In large quantities, ingestion of hexavalent chromium compounds can result in acute gastroenteritis, vertigo, gastrointestinal hemorrhage, convulsions, ulcers, kidney damage or failure, and liver damage or failure. Acute skin exposure can cause burns, liver damage or failure, kidney damage or failure, and anemia. Effects of chronic skin exposure include dermatitis, hypersensitivity reactions, eczema, and kidney or liver damage. Hexavalent chromium is classified by IARC as a known human carcinogen (Group 1).

Workers have the highest risk of adverse health effects from hexavalent chromium exposure. The industries with the greatest risk of occupational exposure are chrome electroplating, stainless steel welding, metal coating and painting, printing, textiles, leather tanning, wood preservation, and cement or masonry work.

The Institute assessed three general categories of use: decorative chrome electroplating; hard chrome electroplating; and chromate conversion coatings. The category of chromate conversion coatings was narrowed further to focus only on passivation of zinc and zinc alloy plated parts and zinc galvanized steel.

Decorative chromium electroplating of consumer and automotive products

Decorative chrome plating is used for consumer applications such as appliances, metal furniture, plumbing fixtures, knobs and hand tools, and for automotive trim. It creates an attractive blue-white finish and helps to reduce tarnishing.

The major advantage of decorative hexavalent chromium is its appearance, especially its blue-white color. It also presents some processing difficulties. These include poor throwing power (a measure of coverage in recessed areas of a part being plated), low resistance to burning during plating, difficulty in removing impurities from the plating bath, problems in rinsing the plating solution from the plated parts, and intolerance to interruptions or variations in the electrical current during plating.

The Institute assessed two alternatives to hexavalent chromium for decorative chrome electroplating: trivalent chromium plating baths, and low temperature arc vapor deposition of trivalent chromium.

- **Trivalent chromium plating baths** use a very similar process to that used in hexavalent plating.
- **Low Temperature Arc Vapor Deposition (LTAVD®)** is a proprietary process in which parts to be coated are exposed to a vaporized metal that condenses on the parts, depositing a thin, solid film.

The Institute assessed health, environmental, technical, and cost criteria for each of these alternatives.

- **Health.** Both options are superior to hexavalent chromium plating from the perspective of carcinogenicity and occupational exposure standards. LTAVD® is superior from the perspective of skin irritation/sensitization, and trivalent chromium baths are either similar or superior to hexavalent chromium baths on this metric.
- **Environment.** Both options are superior to hexavalent chromium plating from the perspective of waste generation. LTAVD® avoids the need for a lead anode; trivalent chromium baths may or may not use a lead anode.
- **Technical criteria.** Criteria of interest include uniformity of coating, adhesion to substrate, hardness, color, and resistance to corrosion and wear.
    - Decorative trivalent chromium plating has many processing advantages over hexavalent chromium plating. Examples of these advantages include superior throwing and covering power; tolerance of electrical current interruptions; low susceptibility to burning; and ease of rinsing and removing impurities. Trivalent chromium plating has a naturally micro-porous structure, which is advantageous for corrosion resistance. In the past, the color of trivalent chromium plating was a disadvantage, but recent developments now make it possible to produce a trivalent plate with an appearance equivalent to that produced using hexavalent chromium.
    - LTAVD**®** operates at room temperature, making it possible to use it on a substrate with a low melting point, such as plastic. By using different combinations of gases and metals, a variety of coatings can be formed. Metals with dissimilar characteristics, such as titanium and aluminum, can be alloyed using this process, creating unique coating materials. Most of the technical assessments of LTAVD**®** have been conducted by the company that holds the patent rights. Findings of these assessments indicate that LTAVD**®** produces a very uniform coating with good adhesion to the substrate, corrosion resistance similar to or better than that of hexavalent chromium, color similar to that produced with hexavalent chromium, and hardness superior to that produced with hexavalent chromium.
- **Cost.** Trivalent plating chemicals are more expensive than hexavalent plating chemicals, although economies of scale are likely to lead to falling prices as trivalent systems increase in popularity. The cost of chemicals, however, is offset by the greater efficiency of the trivalent

process and greatly reduced costs for exposure control and disposal. One study estimated that the volume of sludge generated by the hexavalent process is about 30 times that of the trivalent process. Another found that hexavalent treatment costs were nearly 10 times that of the trivalent process. While cost information for LTAVD® has not been published, the process is being used by several major manufacturers of consumer hardware, indicating that it is commercially viable. Since a wide variety of gases and metals are used, material costs also would vary accordingly. A major operating cost would be energy. Waste treatment costs are likely to be minimal.

Hard chromium electroplating of industrial components

Hard chrome plating, also known as functional or industrial chrome, typically is thicker than decorative chrome. It is used on industrial components that must perform under demanding conditions such as high temperatures, and repetitive grinding and impact forces (such as aircraft engines and landing gear, hydraulic cylinders, and drill bits). Unlike decorative chrome, appearance usually is not an important issue.

The two main reasons for using hard chrome are to provide wear and corrosion resistance, and to rebuild worn components to precise dimensions. It has a low coefficient of friction, is hard and heat-resistant, adheres well to substrates of various geometries, and provides corrosion resistance.

Hard chrome plating suffers from a number of technical limitations. The plating process involves numerous steps, which may need to be repeated in order to achieve an adequate coating. The coating can be brittle, leading to failure or reduced corrosion resistance. It can also be difficult to achieve even plating thickness.

The Institute assessed six processes that can serve as alternatives to hard chromium electroplating:

- **Thermal sprays** include high velocity oxy-fuel (HVOF) and plasma sprays. Thermal spray is a coating process in which wire or metallic powder is melted by a high temperature flame and sprayed as particles or droplets onto a substrate.
- **Weld facing** is a dry method of joining a hard coating, edge, or point to a metal or alloy substrate to improve its resistance to abrasion, corrosion, heat or impact. It also is used to restore worn surfaces.
- **Heat treatments and plasma nitriding** methods use heat to diffuse elements into the top surface of a substrate metal to form an alloy or layer with desired properties.
- **Nanocrystalline coatings** use electrodeposition, vapor deposition, or spray conversion processing to deposit very small grains of crystalline alloys on a metal substrate.
- **Vapor deposition:** In *physical vapor deposition (PVD)***,** parts to be coated are exposed to a vaporized metal that condenses on the parts, depositing a thin, solid film. Types of PVD processes include ion plating, vacuum evaporation, thermal evaporation, electron beam evaporation, and sputter deposition. *Chemical vapor deposition (CVD)* is similar to PVD, but uses gases that combine on a hot surface to form the hard coating.
- **Functional trivalent plating**: The Faraday Technologies' Faradaic™ process is similar to the wet hexavalent plating process, with the capability to plate a thick, functional chromium coating using a trivalent chromium plating bath. It is intended as a "drop-in" alternative to hexavalent baths.

Some of these categories include several related processes that differ in their functional details. In addition, the categories often overlap to a certain extent, so that a given process may be classified differently in different sources. Surface coatings of various materials, typically other metals, alloys, and metal carbides or nitrides, can be applied using these processes. Coatings that may be used to replace hard chrome include those based on titanium, tungsten, cobalt, aluminum and silicon.

For each of these alternatives, the Institute assessed human health, environmental, technical, and cost criteria.

- **Health.** All the alternatives are superior to hexavalent chromium from the perspective of carcinogenicity. However, there are health hazards associated with the alternatives as well. For example, thermal sprays may contain cobalt powder, which is classified as possibly carcinogenic to humans. This is an improvement over hexavalent chromium, which is classified as a known human carcinogen.
- **Environment.** All the alternatives are superior to hexavalent chromium from the perspective of waste generation.
- **Technical criteria.** All of the alternatives have the potential to offer equivalent or better performance compared to hard chrome plating, although several have some limitations in their application. However, given the range of alternative processes and coating materials, there is likely to be at least one alternative that can meet the technical requirements of every hard chrome plating application.
- **Cost.** Many of the alternatives require a significant capital investment. On the other hand, the manufacturers of these systems claim that operating costs are significantly reduced. In some cases, new equipment may pay for itself within a few years through reduced operating costs.

Passivation of zinc plated parts and zinc galvanized steel

Passivation is a surface treatment that provides resistance to corrosion. The protection is afforded by a film or thin coating that interacts with the underlying metal. Hexavalent chromium is a standard passivating chemical for zinc and zinc-alloy plated parts, and zinc galvanized steel.

In passivation with hexavalent chromium, zinc plated parts are dipped into an acidic solution containing a mix of chemicals. The solution reacts with the plating to form a film of zinc chromate and other chromate compounds in both the trivalent and hexavalent state. This is referred to as a "conversion coating" because the hexavalent chromium solution converts the surface to zinc chromate. The hexavalent chromium reacts with the metal, forming an inert trivalent chromium layer with "releasable" hexavalent chromium ions that inhibit corrosion. The residual hexavalent chromium in the film will repassivate any areas on the surface that become compromised due to chemical or mechanical damage to the area. This property is referred to as "self-healing."

The Institute selected three alternatives for study: molybdates, trivalent chromium compounds, and mineral tie-coat.

- **Molybdate-based coatings** inhibit corrosion by forming a protective oxide layer on metal.
- **Trivalent chromium passivates** exist in several types. They vary in appearance, performance characteristics, thickness of the coating, and other characteristics.

- **The mineral tie-coat** process is a patented method of applying a thin mineral film on the surface of metal parts. It involves cleaning and conditioning the surface to be plated, immersing it in a sodium silicate solution, and then electrodepositing a mineral coating. The reaction between the coating and the metal surface forms a new protective surface.

For each alternative, the Institute assessed health, environmental, technical, and cost criteria.

- **Health.** All the alternatives offer significant improvements over hexavalent chromium from the perspective of carcinogenicity and occupational exposure. Chemicals used in the trivalent chromium passivation process may pose skin irritation/sensitization hazards similar to those used in the hexavalent chromium process.
- **Environment.** All of the alternatives offer significant improvements in terms of their environmental impact, although chemicals used in some molybdate formulations are toxic to aquatic life.
- **Technical criteria.** Performance criteria of interest for passivation of zinc include corrosion resistance, heat resistance, torque/tension performance, and appearance.
  - Several technical evaluations have concluded that molybdates do protect against corrosion, but do not perform as well as hexavalent chromium passivation on this metric. Trivalent chromium may be inferior, equal, or superior to hexavalent chromium on this metric, depending on the thickness of the coating, the plating method, the additives, and whether a topcoat was used. According to the manufacturer, mineral tie-coat has superior corrosion resistance when used with a topcoat.
  - Trivalent chromium compounds do not have the "self-healing" properties of hexavalent chromium, and require a sealer/topcoat in order to offer the same level of corrosion resistance. The manufacturer of the mineral tie coat process claims that it is equal to or better than hexavalent chromium in corrosion resistance (with topcoat), heat resistance, and torque/tension performance.
  - Trivalent chromium coatings differ in appearance from hexavalent chromium films. For most applications, color is a matter of user preference rather than of performance. In cases where a specific color is required, topcoats or sealers can be used to achieve the desired effect.
  - The molybdates offer better heat resistance than hexavalent chromium.
- **Cost.** Little cost information is available for these alternatives. One analysis indicated that a molybdate-based process would be similar to a hexavalent chromium process in terms of labor and capital, more expensive for chemicals and energy, and less expensive for waste processing.

DEHP

Di (2-ethylhexyl) phthalate (DEHP) is a synthetic organic chemical that is used primarily as a plasticizer to impart flexibility to rigid plastics such as PVC. It belongs to the class of chemicals known as phthalates, which are used primarily as plasticizers in PVC plastics in a range of applications. DEHP is used in a wide variety of flexible plastic products.

DEHP is classified by the U.S. EPA as a probable human carcinogen (Class B2). In 2000, IARC changed its classification for DEHP from Group 2A ("possibly carcinogenic to humans") to Group 3 ("cannot be classified as to its carcinogenicity to humans"). Animal studies have found that DEHP is toxic to the male reproductive system. When DEHP is metabolized in the human body, it produces compounds that are likely to be reproductive toxicants.

DEHP can be released to the environment during its production, distribution and incorporation into PVC. DEHP is also released when PVC material is heated or comes into contact with certain media. DEHP is not chemically bound into the polymer matrix and therefore can migrate out of the polymer. It is especially likely to migrate out of the polymer in the presence of fatty solutions. Indoor releases of DEHP to the air from plastic materials, coatings, and flooring in home and work environments can lead to higher indoor levels than are found in the outdoor air.

Use of DEHP in flexible PVC medical devices is a significant source of exposure, especially in neonatal care. The National Toxicology Program (NTP) has expressed serious concern about reproductive toxicity in male infants who are exposed to DEHP in medical care. The Food and Drug Administration has recommended that health providers consider using alternatives to DEHP-containing medical devices when high-risk procedures are to be performed on male neonates, pregnant women who are carrying male fetuses, and peripubertal males.

The Institute assessed alternatives to DEHP in PVC in three categories: medical devices for neonatal care; resilient flooring; and wall coverings. Because DEHP is used primarily as a plasticizer in PVC plastics, two types of substitutions may be relevant: substitution of an alternative plasticizer for use with PVC, or use of a different material that does not require addition of a plasticizer. For each application, the Institute examined alternatives in both categories.

Resilient flooring

Resilient flooring is defined as tile and sheet materials that have the ability to return to their original form after compacting. The Institute assessed alternative plasticizers for use in PVC flooring, as well as alternative flooring materials.

Alternative plasticizers

The Institute assessed four alternative plasticizers for use in resilient flooring: di (2-ethylhexyl) terephthalate (DEHT), di isononyl phthalate (DINP), dipropylene glycol dibenzoate (DGD), and di (2-ethylhexyl) adipate (DEHA).

- **Health.** All the alternatives appear to be superior to DEHP from the perspective of reproductive toxicity, although some evidence exists that DEHA may be toxic to the developing fetus. None of the alternatives has been classified as to carcinogenicity in humans, but there is evidence that DINP is carcinogenic in rodents.
- **Environment.** All of the alternatives are less bioaccumulative than DEHP. DEHA is less persistent in sediment and less toxic to fish than DEHP; the other plasticizers are similar to DEHP for these parameters.
- **Technical criteria.** Technical parameters of interest for alternative plasticizers in resilient flooring include volatility, ease in compounding, tensile elongation, compatibility with PVC, and loss of plasticizer during manufacture and use. All the alternatives are comparable with DEHP from the perspective of volatility and tensile elongation. All except DEHT are comparable to DEHP with regard to compounding, and all except DEHA are comparable to

DEHP with regard to PVC compatibility. DINP has greater emissions during use, DEHA is inferior with regard to emissions during both manufacturing and use, and DGD has unknown properties on this metric.

- **Cost.** All the alternative plasticizers are comparable in cost to DEHP for resilient flooring applications on a functional equivalence basis.

Alternative materials

The Institute assessed three alternative flooring materials: natural linoleum, cork, and polyolefin.

- **Health.** Many studies have examined the human health and environmental implications of choice of flooring materials. Most of these studies examine the entire life-cycle of the product, from production to disposal. In general, these analyses favor the alternatives over DEHP/PVC flooring. Polyolefin flooring has the advantage of very low VOC emissions during use.
- **Environment.** Linoleum and cork are derived from sustainable materials and are biodegradable, making them superior to DEHP/PVC on these metrics. Cork offers the additional advantage that it can be installed without the use of adhesives. Linoleum has less impact on energy use from a life cycle perspective than DEHP/PVC flooring.
- **Technical criteria.** Technical criteria of interest for flooring applications include the availability of a range of colors and patterns; ease of maintenance; and recyclability. Linoleum and polyolefin flooring materials offer a range of colors and patterns that make them similar to DEHP/PVC in this regard, while cork is more limited in this respect. Ease of maintenance is generally similar across all the options. Polyolefin flooring is recyclable; linoleum and cork are not.
- **Cost.** The alternatives are generally similar to DEHP/PVC in purchase and installation cost, although costs vary depending on application. All the alternative materials have a longer expected life span than DEHP/PVC, further decreasing the overall cost.

Medical devices for neonatal care: sheet and tubing applications

Two distinct categories of medical devices used for infants in neonatal intensive care facilities were the focus of this study: bag/sheet devices, and tubing. The Institute investigated both alternative plasticizers and alternative materials for this application.

Alternative plasticizers

The Institute assessed five alternative plasticizers for use in medical devices.

- **Trioctyl trimellitate (TOTM)** is a clear, oily liquid that is a high production volume plasticizer in the US. In the medical device industry, TOTM is currently used primarily in blood and bag infusion sets.
- **Di (2-ethylhexyl) adipate (DEHA)** has properties that make it a useful plasticizer for materials used to store medical solutions that must be kept cold.
- **Butyryl trihexyl citrate (BTHC)** is a plasticizer specifically designed for use in medical articles, especially blood storage bags.

- **Di (isononyl) cyclohexane-1,2-dicarboxylate (DINCH)** is the hydrogenated product of the corresponding di C9 phthalate ester (DINP).
- **Di isononyl phthalate (DINP)** is currently used as a plasticizer in medical tubing devices.

TOTM, DEHA, BTHC, and DINCH are applicable for use in bag/sheet devices. Based on their elastic recovery properties, DEHA is also applicable for use in tubing, and DINP was assessed for use in tubing only. For each of these alternatives, the Institute assessed health, environmental, technical, and cost criteria.

- **Health.** All the alternatives are superior from the perspective of carcinogenicity and reproductive toxicity, although there are grounds for concern about DINP and DEHA, as noted above. The alternatives are generally superior with regard to skin, eye, and respiratory irritation, with some exceptions.

  A key issue associated with potential health effects is the ability of a plasticizer to exude from the polymer matrix as well as its potential to produce metabolites of concern. DEHP is lipid soluble and therefore is likely to exude out of the polymer when exposed to a lipid-soluble solution. TOTM, BTHC and DINCH appear to be less likely to migrate out of the polymer in the presence of lipid-soluble medical solutions. DINP appears to be similar to DEHP in this regard, and the potential for DEHA to migrate is not well defined.

  Little information is available on the health effects of metabolites associated with the alternatives assessed. The exception is BTHC, which can be metabolized to butyric acid, a chemical that is associated with negative impacts on the GI tract, liver and skin.

- **Environment.** All the alternatives are equally or less persistent in sediment compared to DEHP (DINCH persistence is unknown). The alternative plasticizers studied are all superior from the bioaccumulative and aquatic toxicity perspectives, with the exception of DINP, which has aquatic toxicity similar to that of DEHP. The aquatic toxicity of BTHC is not known.
- **Technical criteria.** Important criteria for both sheet/bag and tubing applications include flexibility when cold, clarity, compatibility with PVC, sterilizability, and plasticizer loss during manufacture and use. In addition, elastic recovery is an important parameter for tubing applications. Some important differences between DEHP and alternatives are noted below:
  - TOTM is inferior on measures of cold flexibility; DEHA is similar; and the other three alternatives are superior to DEHP on this measure.
  - DEHA is less compatible with PVC than DEHP.
  - BTHC is not steam sterilizable, while DINP tolerates steam sterilization better than DEHP. The sterilizability of DINCH is not known.
  - TOTM, BTHC, and DINCH are superior to DEHP on measures of plasticizer loss during use. DEHA and BTHC are inferior to DEHP on measure of plasticizer use during manufacture.
- **Cost.** Costs of DEHA and DINP are similar to those of DEHP, while the other alternatives are more expensive.

Alternative materials

The Institute evaluated five alternative materials for medical devices: ethyl vinyl acetate (EVA), polyolefins (polyethylene and polypropylene), glass, silicone, and polyurethane. Some of these could replace DEHP/PVC sheets, while others could replace DEHP/PVC tubing.

- **Ethyl vinyl acetate (EVA)** is a copolymer blend of vinyl acetate, ethylene, and ethyl acetate that has been used for many years in medical sheet applications. EVA bags are also used for custom mixing of drugs by pharmacies.
- The **polyolefins** polyethyelene (PE) and polypropylene (PP) are widely used compounds that are valued for their flexibility, transparency and toughness.
- **Glass** was commonly used to store medical solutions prior to the extensive use of plastics.
- **Silicone** is a synthetic rubber that can be used in medical tubing. Silicone tubing is translucent, biologically inert, and inherently flexible.
- **Thermoplastic polyurethane (TPU)** is used in tubing applications.

The Institute assessed health, environmental, technical and cost criteria for each alternative.

- **Health.** All the alternative materials are superior to DEHP/PVC from the perspective of leaching plasticizers with known health concerns, since none of the alternatives utilize plasticizers. While rigid and more difficult to handle due to the potential for breakage, glass is the most inert material available on the market today for health care.
- **Environment.** All the alternative materials are superior to DEHP/PVC materials plasticized with DEHP in the sense that they do not generate hazardous chlorinated organic compounds when incinerated. However, there is significant variation among the alternatives in level of toxicity over the life cycle of the product. Manufacture of TPU involves use of diisocyanates that are listed on the Massachusetts Science Advisory Board's list of more hazardous chemicals. Incineration of TPU also releases hazardous chemicals including isocyanates and hydrogen cyanide. On measures of recyclability, glass is far superior to PVC containing DEHP; other alternatives are equally or more difficult to recycle compared with DEHP/PVC.
- **Technical criteria.** Using materials that are inherently flexible eliminates one of the key problems with DEHP/PVC, the potential for the material to become brittle due to loss of plasticizer. Therefore, the alternatives may have longer shelf lives than their DEHP/PVC counterparts and the possibility of leached plasticizer entering the body is eliminated. Other performance criteria of interest for these uses include elastic recovery, cold flexibility, sterilizability, gas permeability, and manufacturability. Some key differences between the alternative materials and DEHP/PVC are noted below.
  - TPU exhibits inferior elastic recovery.
  - Only silicone is superior to DEHP/PVC from the perspective of cold flexibility. Glass is not flexible.
  - Neither EVA nor polyolefin is appropriate for steam sterilization.
  - Manufacturability (i.e., the ease with which the material can be transformed into the finished product) is superior for glass, and inferior for EVA, silicone and TPU.

- **Cost.** Currently raw material prices and relative use costs for the alternatives vary relative to DEHP/PVC. However, costs of the alternatives are changing in response to increasing demand for and supply of DEHP- and PVC-free medical devices. Technical differences among materials can also be a source of cost savings. For example, EVA film can be manufactured at a thinner gauge than similar PVC film, thus reducing the per-item cost. For tubing applications, silicone and TPU can be used for longer periods of time than PVC/DEHP, thereby reducing the cost differential. Large hospital chains are also driving market changes, and cost reductions, by specifying PVC- or DEHP-free materials in their purchasing contracts.

Wall coverings

DEHP/PVC (vinyl) wall coverings are used in both commercial and residential settings for decorative and protective purposes. Vinyl wall coverings are popular because they are available in a wide array of patterns and colors and are both durable and scrubbable.

It is worth noting that there are viable process alternatives to vinyl wall coverings, including painted wall surfaces or using different wall materials (such as wood paneling). They differ significantly from wall coverings in terms of aesthetics, but can be functionally equivalent. These process alternatives were not included in the assessment.

Alternative plasticizers

The Institute assessed two plasticizer alternatives for use in wall coverings: DEHA and DINP.

- **Health.** As previously discussed, DEHA is potentially toxic to the developing fetus and DINP has been found to cause cancer in laboratory animals. The potential for exposure to DEHA is greater than for DEHP.
- **Environment.** DEHA is less persistent in sediment than DEHP, and DINP is similar to DEHP on this parameter. Both are less bioaccumulative than DEHP. DEHA is less toxic to fish than either DEHP or DINP.
- **Technical criteria.** Criteria of interest for wall coverings include volatility, compounding, tensile elongation (life of product), compatibility with PVC, and emissions (during manufacture and use). DINP is similar to DEHP on all measures. DEHA is inferior on measures of volatility, PVC compatibility, and emissions during manufacture and use. Compared with DEHP, DINP has better high temperature performance and extraction resistance, which improves is processability.
- **Cost.** Both plasticizers are similar to DEHP in cost per pound applied. Compared with DEHP, DINP processing emits lower levels of plasticizer mist from process equipment. As a result, less plasticizer is lost to the air and more retained in the product, yielding overall cost savings.

Alternative materials

The Institute assessed five categories of alternative materials: glass woven textiles, cellulose/polyester blends, wood fiber/polyester blends, biofibers, and polyolefins.

The Institute evaluated health, environmental, technical, and cost criteria for each of these alternative materials.

- **Health.** The primary concern with DEHP in wall coverings is exposure during manufacture and use. No plasticizer is emitted during manufacture or use of the alternative materials, but there may be other volatile organic emissions. In particular, the glass textile and polyolefin alternatives have similar potential VOC exposures compared to DEHP/PVC. Little information on exposure associated with the other materials was available.
- **Environment.** All the alternative materials except the polyolefins are derived from more sustainable materials than DEHP/PVC. Some offer the advantage of being recyclable and one alternative material (wood pulp/recycled paper) is compostable. Two of the alternative materials (BioFibers and polyolefins) are routinely coated with Teflon® finish, which may pose occupational and other hazards.
- **Technical criteria.** All the alternatives are similar to DEHP/PVC in ease of maintenance. Wood fiber/polyester and cellulose/polyester alternatives offer a range of colors and patterns similar to those available with DEHP/PVC.
- **Cost.** Most of the alternatives are comparable in price to high-end DEHP/PVC wall covering products, but are much more expensive than low-end vinyl.

Economic Assessment

Financial considerations are discussed within each alternatives assessment. The information presented for each case varies according to context. For example, the price of materials is an important parameter for some cases, while operation, maintenance, or disposal costs may be salient for others.

Specific lessons that can be drawn from the alternatives assessments conducted here include the following.

- Some alternatives can be adopted without any adverse effect on Massachusetts employment or competitiveness. The formaldehyde alternatives assessment, for example, shows that elimination of formaldehyde dry sterilant from use in Massachusetts hair salons would produce savings and make sanitation standards at Massachusetts hair salons consistent with those in the rest of the country. Similarly, Massachusetts schools could adopt alternatives to formaldehyde-fixed dissection specimens without increasing costs.
- Massachusetts manufacturers could gain market share through adoption of some alternatives. For example, some Massachusetts firms are working to produce DEHP-free medical devices. With growing demand for such devices, firms may have opportunities for growth in this area.
- Some alternatives require capital investment at the outset. For some technologies, this investment will pay for itself over time in reduced operating costs.
- In some cases, alternatives are more costly at this time (*e.g.*, PCE vapor degreasing solvent alternatives) and for many no firm cost conclusions can be reached without more information.

In addition, the Institute convened a group of economic experts to assess potential state-wide implications of adopting alternatives for employment in the Commonwealth and competitiveness of Massachusetts firms. The panel of experts worked with TURI to develop a framework for analysis of the economic implications within Massachusetts of alternatives adoption. This framework will assist users in analyzing likely economic impacts by clarifying the situational characteristics and factors that determine the outcome. Characteristics that may help to determine the economic implications of alternatives adoption include the size of the Massachusetts market in comparison with other markets, price sensitivity of consumers, nature of barriers to adoption, capacity of the workforce, and availability of useful and timely information.

Broader conclusions that emerged from the Institute's literature review and consultation with experts include the following.

- First, there is strong evidence that adoption of safer alternatives can produce economic benefits. This is a lesson from the experience of the TURA program, the literature on this topic, and some of the sectors considered in this report.
- There are some cases in which substituting chemicals or processes may have negative effects on some firms, even if there is a positive effect on the state economy more generally.
- There are many opportunities for government to support a positive economic outcome and to mitigate any negative effects for individual firms. In some instances, targeted assistance to industry can facilitate adoption of safer alternatives that will yield employment and competitiveness benefits over time.

Conclusions

The detailed information provided in this report should serve as a valuable resource for anyone interested in understanding the alternatives to the five chemicals that were examined in this study. The report is designed to be useful to policy makers, industry, public health and environmental professionals and advocates, and other stakeholders. In every case, at least one alternative was identified that was commercially available, was likely to meet the technical requirements of many users, and was likely to have reduced environmental and occupational health and safety impacts compared with the base chemical.

The active involvement of all stakeholders was key to the success of this project. Their expertise, willingness to collaborate and share perspectives, and review of the report were invaluable. The involvement of a wide range of stakeholders throughout the project resulted in a more accurate assessment, more valuable results, and increased understanding of the issues, challenges and perspectives among stakeholders. Stakeholder contributions to this project also revealed in detail the substantial investment firms have made in developing safer products. For example, efforts to reduce the negative impacts of formaldehyde in wood products have succeeded in producing formulations with greatly reduced off-gassing. Similarly, years of effort have been devoted to developing reliable lead-free electronics.

Many promising alternatives were identified during this study. Some of these will require further work to determine their practicality and applicability for specific applications. Such work will speed up the adoption of these alternatives, and could include detailed discussions with vendors and users, independent laboratory testing of technologies, pilot-scale industrial installations, supply chain workgroups and demonstration sites. The Institute has had success using these approaches for industrial toxics use reduction, and believes that there are many parallels for small businesses and consumer products.

The Institute's experience with this study has also yielded important lessons about the methodology of alternatives assessment. The experience of the Institute and the information contained in this report indicate that alternatives assessment is a useful approach to organizing information about chemicals and alternatives. The Institute encourages readers to build on the work that has been done in this study, both by conducting alternatives analyses on other chemical uses, and by working to refine and streamline this methodology.

Finally, this study will have been a success if it spurs discussion and debate. It is the Institute's hope that the information in this report will serve as valuable source material for those discussions.