Migration Models - Comparison of PVC, PET and PLA Diffusivity, Combined with a Production Cost Model for Westridge Laboratories

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Approval Page

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Abstract

This project has two parts: [1] a migration and diffusivity model for candidate plastics used in containers, and [2] a product cost model for Westridge Laboratories (Santa Ana, CA).

Diffusion modeling is a useful tool to predict migration of polymer constituents into exposed liquids. Polyvinyl chloride (PVC), polyethylene terephthalate (PET) and polylactic acid (PLA) were studied to estimate production costs, and component migration into water-based liquids from plastic containers. Bis (2-ethylhexyl) phthalate (DEHP), antimony trioxide, and stannous octoate, are components of concern in the three candidate polymers, respectively. Normal detection limits for these constituents are about 1 - 10 ppb, so they are often difficult to measure at ultra trace levels after migration (< 1 pptr). This study uses modified Fick's First and Second Laws, and a modified Arrhenius equation, to develop a working migration model. PLA is the only biodegradable candidate polymer. With properties similar to PET (*e.g.,* optical clarity and inertness), PLA could be a preferred PET alternative. According to this model PVC has higher migration rates at higher temperatures for chosen analytes, than either PET or PLA. However at lower temperatures PET has the highest migration rate. Since PLA is somewhat new, there is a paucity of study data. Reasonable range assumptions were made for PLA diffusion coefficients. PET and PLA show similar migration curves.

Keywords – Migration, Polyvinyl Chloride, Polyethylene Terephthalate, Polylactic Acid, Antimony Trioxide, Bis (2-ethylhexyl) Phthalate, Stannous Octoate, Diffusivity, Cost Model

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Introduction

Plastic is available to every country in the world, and is used in almost every profession and application, from cosmetics, to building equipment, to children's toys and most importantly for food and water packaging. Plastic containers must be approved by the Food and Drug Administration (FDA) to be used in food applications. One of the most important predictive techniques used by FDA is migration modeling. By definition migration is the movement of chemical constituents within a plastic matrix. In other words migration is how far certain plasticizers or additives move within a plastic during defined time periods under known conditions of temperature and composition.

This study looked at the migration of bis (2-ethylhexyl) phthalate, antimony trioxide and stannous octoate, respectively, in polyvinyl chloride (PVC), polyethylene terephthalate (PETE/PET) and polylactic acid (PLA). These polymers represent three different categories, [PVC] a polymer that has been recently shown to have negative health effects and has been banned from some children's toys, [PET] a polymer that is currently undergoing multiple types of migration testing and is most often used for food and liquid packaging, and [PLA] a new polymer that has yet to be tested by FDA, but offers a biodegradable alternative to currently used polymers.

Migration models used in this study are hypothetical; however, they give a useful estimation of rates for constituents migrating into contained liquids.

Along with the migration study, this report also contains a cost model for production costs at Westridge Laboratories Inc. Westridge is a lubricant manufacturer located in Southern California. The current Westridge manufacturing system is efficient and functional, yet there is no data cost accounting. This lack of information about manufacturing costs makes it difficult for the company to predict profitability and manage production. Westridge Labs would like to have a working cost model for new and current products. By understanding their manufacturing costs, Westridge will be able to develop effective cost accounting procedures. The challenge product was their best selling lubricant, their 2.5-ounce "ID Millennium" lubricant. The cost model developed

for a 2.5 ounce bottle of ID Millennium can be applied to other bottled products due to the fact that the Westridge manufacturing process has similar steps between existing and proposed new products.

The cost model relates existing economic factors within the company to estimated production cost profiles. While analyzing Westridge's process, allocation of resources was determined, and potential improvements. A company goal is to reduce costs while maintaining a high quality product. Along with cutting costs, the company will need to measure cash flow and study areas of excess cost. The purpose is to discover problem spots and offer money saving solutions. A sample cost model (Appendix A) is attached to this document, and an associated Excel™ data file was developed that tracks production, costs and profitability for Westridge.

Background

This study required in depth knowledge of the three candidate polymers: polyvinyl chloride (PVC), polyethylene terephthalate (PET) and polylactic acid (PLA). The migration modeling focused on the migration rates of potentially harmful polymer constituents; bis (2-ethylhexyl) phthalate, antimony trioxide, and stannous octoate.

The cost model involved a complex direct time study (Appendix B) and an understanding of Westridges' products and company.

Polyvinyl Chloride

Polyvinyl chloride (PVC) is used in many rigid applications today such as window framing, roofing sheets, cable insulation and floor coverings. It is also used in toys and packaging. Although 84% of PVC is used for rigid packaging the remaining 16% is used in flexible applications many that could lead to human contact, or contact with human foods. The addition of plasticizers to PVC allows the polymer to be flexible, but certain plasticizers and catalysts can be hazardous if they migrate into contained substances[1].

Bis (2-ethylhexyl) phthalate (DEHP) is the main plasticizer used to create flexibility in PVC[2]. Raw materials for PVC include petroleum and rock salt. Petroleum is the raw material for ethylene, while rock salt yields gaseous chlorine through electrolysis. The next step is to combine ethylene and chlorine to create ethylene dichloride (EDC)[3]. As EDC decomposes it creates vinyl chloride and hydrochloric acid. Vinyl chloride is then polymerized using different approaches such as suspension or emulsion. The process of manufacturing polyvinyl chloride is shown below (Figure 1)[3].

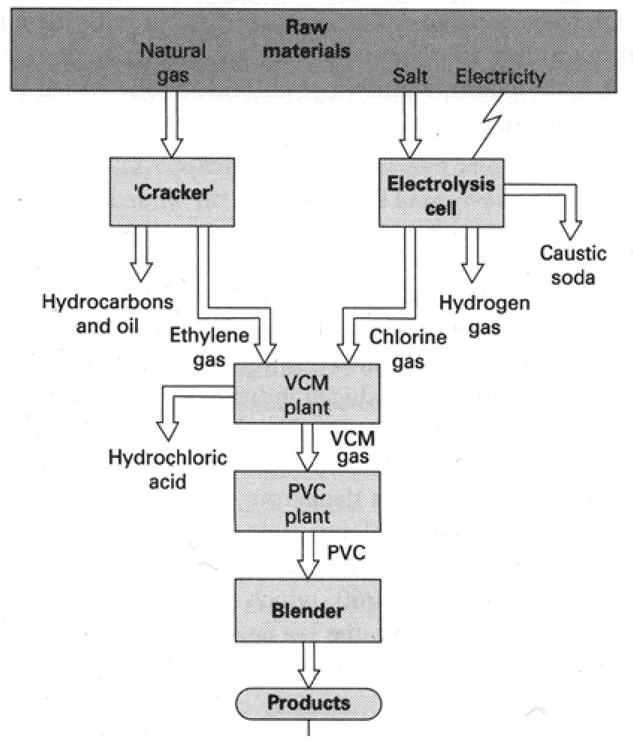


Figure 1. Chemical Process for Manufacturing PVC

Although PVC is created from natural raw materials such as petroleum and salt, it is difficult to recycle. Less than 1% of all the polyvinyl chloride produced is recycled. This means that most PVC ends up in landfills or in general recycling plants that cannot process PVC. As the world increases PVC production, we have yet to discover a way to remove it from waste streams or successfully recycle PVC for alternate uses.

Bis (2-ethylhexyl) Phthalate

Bis (2-ethylhexyl) phthalate (DEHP) is the most commonly used plasticizer and has been the subject of many environmental and human exposure controversies[4]. DEHP can enter the environment in various ways, through manufacture, from landfill run off, and contamination of groundwater near landfills. DEHP is difficult to break down and does not evaporate; so small amounts are released into air, natural water, or soil[5.] Most DEHP contamination that humans receive is through flexible plastic applications such as children's toys,

clothing, wire coatings, electronics and piping. DEHP can also be used in a wide variety of medical devices such as the plastic tubing for intravenous transfusions.

The United States Environmental Protection Agency (EPA) set a permissible safety limit of 4 ug/L of DEHP released into water. EPA estimates that approximately 0.25 mg/day DEHP migrates into our food through PVC containers. EPA has reported acute health effects in humans and chronic health effects in animals from DEHP. Acute risks include gastrointestinal distress as well as kidney and liver distress. Although chronic risks have yet to be found in humans, EPA cites animal studies with increased lung and liver weight gain due to DEHP exposure[6]. EPA is still conducting studies to determine if there are chronic effects on humans.

DEHP is also classified as group B2, a probable carcinogen by EPA. Currently EPA uses mathematical models similar to the computations in this study to determine risk parameters. In 2005 the European Union (EU) voted to permanently ban the use of phthalates in children's toys and childcare articles since DEHP can be up to 40% by weight in PVC formulations. With bans on many plasticizers like phthalates, there has been a push for new plastics, which are safer for children as well as food product exposures[7]. Bisphenol A is a plasticizer used in polycarbonate bottles. In September 2010, Canada became the first country to declare BPA as a toxic substance[8]. In the EU and Canada, BPA use is banned in baby bottles.

Polyethylene Terephthalate

Polyethylene terephthalate (PET) is well known for its use in beverage bottles such as water and carbonated soft drinks[9]. PET is also used in various food applications such as microwaveable food trays and containers. PET is currently the most recycled plastic in the United States; with approximately 28% of all PET produced being recycled[9]. Special recycling plants called Material Recovery Facilities (MRF) recover PET. These facilities create PET flakes to be used in new PET pellets, sheets, bottles and fibers[10].

The process of making polyethylene terephthalate starts with the creation of two raw materials, ethylene glycol (EG) and purified terephthalic acid (PTA). These two chemicals react (Figure 2[11]) to create an intermediate monomer bis- (2-hydroxyethyl) terephthalate (BHET). This intermediate monomer is then polymerized with antimony trioxide catalyst to create polyethylene terephthalate resin.

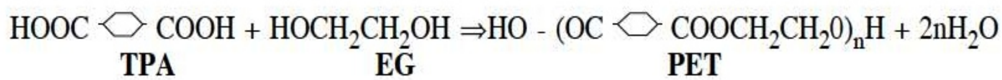
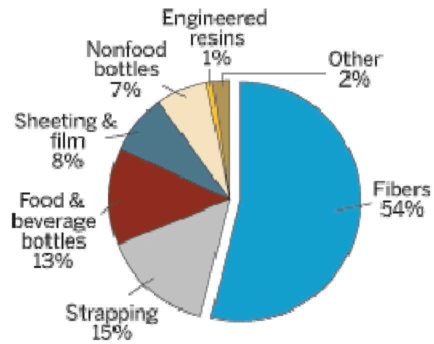


Figure 2. Chemical Reaction to Make PET

Currently PET is encouraged by the FDA because of its low migration rates and good heat resistance. This has led to the growth of PET in food applications to replace other fibers and films (Figure 3)[12].

2008



2010

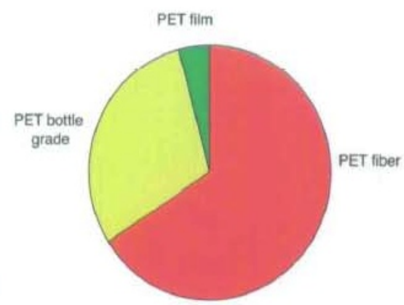


Figure 3. Comparison of PET Uses from 2008 to 2010

With the growing use of PET for food packaging and bottling applications it is important to understand possible health effects with human contact.

Antimony Trioxide

Antimony trioxide (Sb_2O_3) is found in air, water, soil, and sediment. It is used mostly in enamels as a pigments, as well as glass, rubber, plastics, adhesives and textiles. Antimony trioxide is present in the earth's crust at levels of 0.2-1 mg/kg, and in seawater at $2x10^{-4}$ mg/kg[13]. Antimony trioxide is processed through smelting ores, and is released to the air in high concentrations (>300ppm) . Antimony trioxide has recently been added to a list of hazardous substances.

EPA set a 6 ug/l Sb_2O_3 safe level for food or liquid esposure. EPA estimates that approximately 100 ug/day are taken in per person in the U.S.[14]. It has been

deomonstrated that antimony trioxide does not bioaccumulate, so it has less chance to occur in food, although antimony trioxide is found both in drinking water and groundwater[14]. EPA has found both long term (up to 7 years) and short-term effects from Sb_2O_3. Short-term health effects include nausea, vomiting and diarrhea, while long-term effects are decreased longevity and altered glucose and cholesterol blood-levels. This data is based on a 0.01mg/L/day exposure[14.] Antimony trioxide has been listed as group "2B" by The International Agency for Research on Cancer (IRAC), meaning that it is a possible carcinogen. Most studies on anitmony trioxide focus on how much Sb_2O_3 is found naturally in food and drinking water through air and soil contamination, not through contamination from plastic containers. This study attempted to show if plastic-bound Sb_2O_3 contributes to the native levels found in contained foods and liquids.

Polylactic Acid

There is one primary manufacturer, producer of polylactic acid (PLA) in the United States, NatureWorks™. This company is a joint venture between Dow Chemical Company and Cargill Inc. NatureWorks™ only began PLA production in 2001, and now has the capacity to produce about 140,000 tons annually[16].

Polylactic acid is an entirely biodegradable polymer, created using corn grown in North America. Since PLA is an environmentally friendly polymer, there is a push to use PLA in more applications. It is currently used in food packaging, film and fiber. PLA polymer could be the first completely degradable polymer, a solution to many of the problems with previous plastics, such as landfill capacity limitations, and ocean contamination.

It is important to understand the PLA production process. Production begins with the synthesis of lactic acid (Figure 4)[17]. This process uses photosynthesis to create starch, and then uses enzyme hydrolysis to convert starch into dextrose, and finally dextrose is fermented to produce 99.5% liquid lactic acid[17].

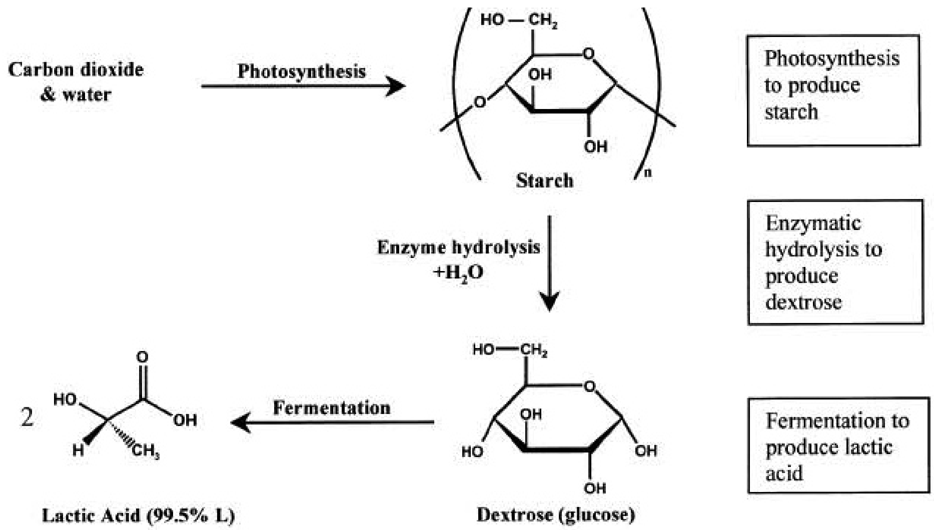


Figure 4. Synthesis of Lactic Acid

The second step in the production of PLA is polymerization of lactic acid (Figure 5)[17]. NatureWorks™ uses open-ring polymerization to create PLA. The first step is water removal from lactic acid using stannous octoate to create a prepolymer called lactide. Lactide is then polymerized in a solvent free ring-opening process that creates polylactic acid pellets. Molecular weight of PLA is controlled by the quality of lactide used. The less water the lactide contains, the purer the PLA, which will produce a higher molecular weight polymer. This is why stannous octoate is an important part of PLA synthesis. Without efficient water removal PLA cannot be formed.

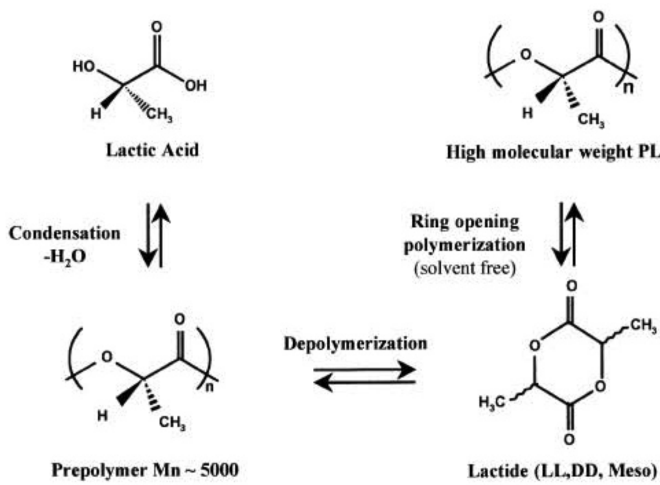


Figure 5. Polymerization of Polylactic Acid

PLA has yet to be added to EPA's regulatory guidelines, but with the growing interest in sustainability PLA will most likely be a research priority for both EPA and FDA. Data provided by NatureWorks™ is listed on the EPA website. The 'carbon footprint' associated with PLA is lower than PVC or PET (see Figure 6)[17]. Ingeo 2009 and Ingeo 2005 are NatureWorks™ current PLA trade names.

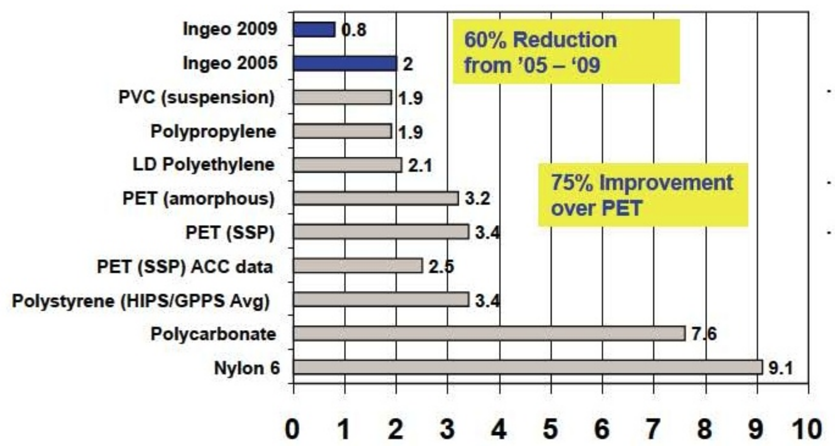


Figure 6. Comparison of Greenhouse Gas Emissions for Various Polymers

Stannous Octoate

Stannous octoate or tin 2-ethylhexanoate (tin EHA) is a reaction catalyst; and it is an additive for paints, coatings and inks. The acid moiety in stannous octoate, 2-ethylhexanoate is known to be biodegradable, with reliable degradation rate data available[18]. Stannous octoate has only recently been used in applications where environmental impacts are important. Toxicity data exists for stannous chloride; however, stannous octoate toxicity has not been extensively studied.

When humans ingest stannous octoate, solubility in the gut is promoted by low pH. Many researchers use tin chloride and EHA as surrogates to predict possible stannous octoate health effects[19], and could include acute gastrointestinal illness as well as nausea, abdominal cramps, vomiting and diarrhea.

Short studies on tin EHA (14 days), show only minor health effects. These studies found that in high doses between 3,400-5,870 mg/kg, tin EHA can cause skin, eye, and stomach irritation. Limited data is avaible on stannous octoate. Dow Chemical Company recently created PLA Material Data Safety Sheet (MSDS) in 2011[20]. There has been no indication that stannous octoate is a carcinogen. Dow has listed stannous octate in reproductive toxicity Catgeory 2, meaning it is toxic to reproductive processes in women.

Cost Model

The purpose of this cost model is to determine areas for cost reduction in Westridge Labs best selling product, ID Millennium lubricant. "Cost models are designed to capture costs in a production line environment, but can be used for other production steps or processes."[21]. The first action was to determine basic manufacturing steps. Costs associated with each step were calculated. Costs can be partially characterized by time intervals to complete each step, the amount of materials required at each step, shrinkage, and labor hours required to complete each step. By understanding the overall procedure, the weight of material used at each step, and material cost, product cost on a unit basis was determined.

After product has been manufactured, shipping costs are taken into consideration. While developing this cost model, the expected cycle length, expected cycle cost, and expected waiting cost was calculated[21]. These parameters help determine the cost of each process step needed to manufacture and distribute the product. A balance between cost and efficiency is found in order to optimize profitability for Westridge Labs. Whether or not Westridge prioritizes minimizing inventory, or prefers being time responsive to orders by expanding inventory, inventory should be taken into consideration by Westridge managers, to determine optimum efficiency for their facility.

A primary Westridge goal is to respond quickly to orders when they are made. This cost model will help to determine the time to execute a work order, and associated unit cost. The cost model allows Westridge managers to determine whether an alternative workflow would be more cost effective. This can be done by changing factors in the time-cost model for individual products[22]. Westridge Labs should consider whether automation is cost effective. Sufficient future sales growth is needed to recover the capital cost of automation equipment.

Methodology

The migration model used in this study was based on Federal Drug and Administration (FDA) guidance. Cost modeling employed direct time-and-motion studies at the Westridge manufacturing floor.

Migration Model

There are many different ways to create a migration model; the one chosen for this report is outlined in Arvenitoyannis and Bosnea's, *Migration of Substances from Food to Packaging Materials to Foods*[23]. In order to create a migration model two separate treatments are needed, [1] application of modified Fick's Laws, and [2] a modified Arrhenius equation. These equations were altered for polymeric migration[23].

A modified Arrhenius equation is used to determine diffusivity(*c.f,* Equation 2 below) , in other words how fast analyte molecules diffuse in the given polymer at a particular temperature. Diffusivity changes for each polymer and at different temperatures.

$$M_t = 2C_o\rho\frac{D_p t}{\pi} \quad [1]$$

$$D_p = 10^4\exp\left[A_p{}^a \times MW - b\left(\frac{1}{T}\right)\right] \quad [2]$$

Where

M_t	= analyte migration through the polymer matrix (mg/dm^3)
C_o	= initial concentration of the migrant additive/plasticizer (mg/g)
D_p	= diffusion coefficient (cm^2/s)
ρ	= density (g/cm^3)
t	= time (s)
A_p	= polymeric constant, accounts for polymer diffusivity
-a	= constant (0.01)
MW	= molecular weight of additive/plasticizer
b	= constant (10450)
T	= temperature (K)

In this instance the model describes how far molecules will move within a given polymer matrix, and analyte concentration at the surface of contained materials (Figure 7)[23].

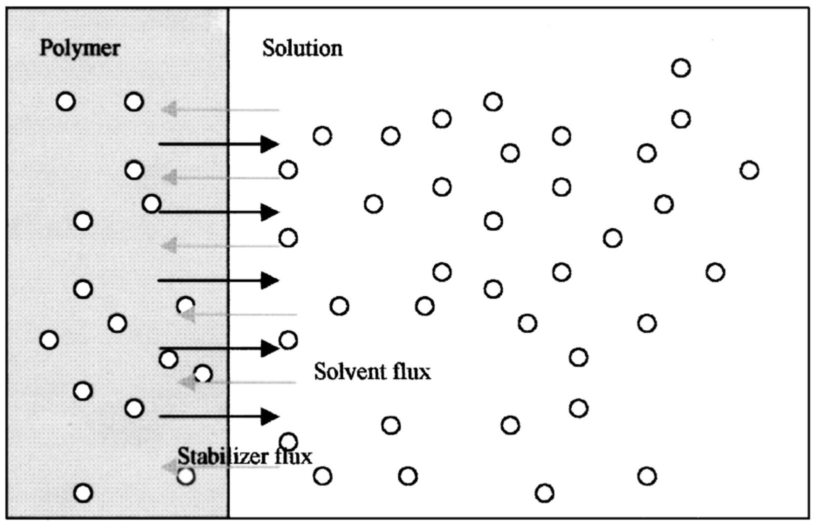


Figure 7. Polymer-Solution Interface, Diffusion Steps

Once equations were established, the next step was to determine which temperatures to use. The three temperatures chosen were: [1] 20°C (68°F), [2] 40°C (104°F), and [3] 121°C (250°F), these reference temperatures are used by FDA and the EU for standard polymer migration tests[24]. These temperatures represent different temperature environments where plastic bottles are stored, or are heated. 20°C (68°F), represents normal room temperature; 40°C (104°F), is storage on a hot day; and, 121°C (250°F) represents direct heat in a microwave oven. FDA also has a reference time for migration tests. The FDA reference standard time is 10 days[24].

Data used in this model were determined using patents as well as previous migration studies and properties pertaining to the specific analytes(Table I).

Table I. Experimental and Estimated Data Used in This Migration Model

	PVC	PET	PLA
D_p (cm^2/s) (20°C)	6.06E-17	8.91E-15	2.86E-15
D_p (cm^2/s) (40°C)	5.90E-16	8.68E-14	2.79E-14
D_p (cm^2/s) (121°C)	5.62E-13	8.26E-11	2.65E-11
20°C (K)	293	293	293
40°C (K)	313	313	313
121°C (K)	394	394	394
A_p	-7	-3	-3
MW	391[25]	291.52[26]	405.10[27]
a (constant)	0.01	0.01	0.01
b (constant)	10,450	10,450	10,450
ρ (g/cm^3)	0.139[25]	0.130[26]	0.127[27]
C_o (mg/g)	0.00346	0.0022	0.0016

Cost Model

The first step in developing a production cost model was to understand Westridge Laboratory's production process. Necessary information included each process step, how long each takes, the amount of material needed throughout the process, and the number of labor hours at each step. Once all the individual factors were determined, each step was weighted. Weights ranked each step, the time it takes, money spent, and hours needed to finish each product unit.

In theory the step that has the most weight will have the greatest impact on product cost. We observed that the steps that require the most labor, and longest times, highly influence product cost. While developing our cost model, some reference estimates were needed; such as expected cycle length, cycle cost, shipping cost, and delay cost[28]. This cost model establishes a balance between cost and efficiency to optimize profitability for Westridge Labs.

To refine the cost model, the time to complete each step was measured using direct-time observations (Appendix B). By observing the manufacturing process, sufficient data was collected to determine the average time to complete each step. Information provided by Westridge Labs for the cost model included hourly wage

for manufacturing employees, overhead costs, and raw material costs. Steps included in the cost model, as stated above, are set up time, labeling time, filling time, capping time, time on conveyer, uncapping time, recapping time, and boxing time. We were able to observe these steps on the manufacturing floor (Figure 8).

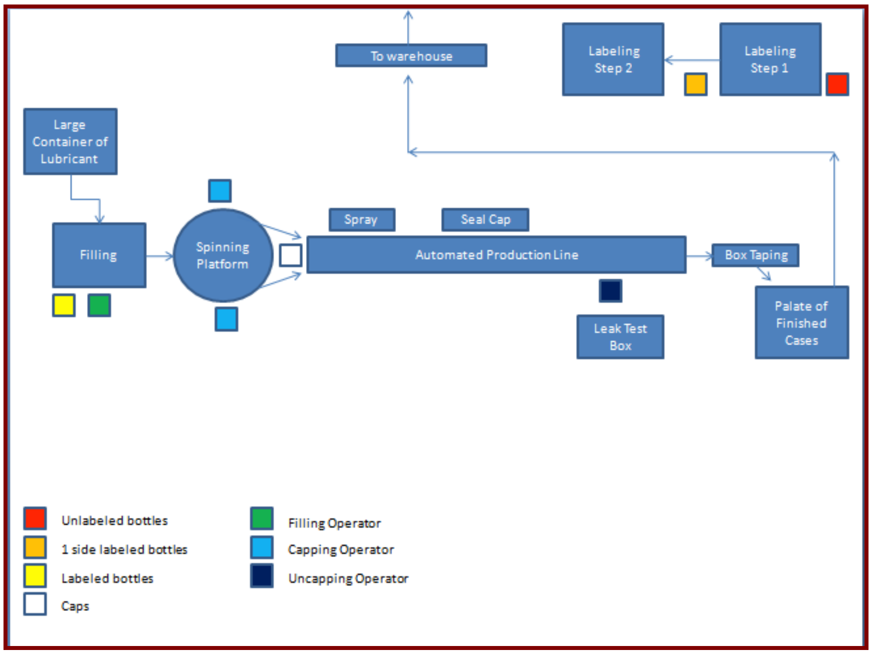


Figure 8. Detailed Layout of Westridge's Manufacturing Floor.

Westridge wanted to answer two questions, "If a batch of 'x' amount of product is ordered, how much will it cost us to make it, and how long will it take to make." To answer the first question, the total time to complete a bottle was calculated by adding the individual steps and summing step costs. The time to complete a bottle was multiplied by the number of bottles in the order times the production cycle time.

Also included in the time to complete a bottle, was a fixed set up time of 20 minutes (*Note – We were unable to observe the set up process, so this is an estimated time based on interviews with manufacturing employees who perform set up*). Once a batch size is selected, the number of boxes needed for that order is

calculated. Time to package product is included in the cost model.

After batch time was calculated, unit cost was considered. These costs included average hourly wage of workers, cost of the raw materials, and overhead costs. Hourly wage of manufacturing staff includes taxes and the cost of employee benefits. By including this information, a cost model was generated to calculate time increments needed per batch of 2.5 ounce ID Millennium product, as well as batch cost. In addition to calculating the total cost and time required per batch, additional information about each step in the process was needed. By using the same process as stated above, the time and cost to complete each step was calculated. By summing the times to complete each step, the time and cost to complete physical steps were found.

Although the ID Millennium lubricant product was used as a reference, this cost model can be applied to other Westridge products[29]. Steps to produce each product are very similar. So, with slight alterations to the cost model, such as adding uncapping and recapping times, refined cost estimates can be incorporated into the model and the cost computed for any new product.

Results – Migration Model

Three graphs are shown below using the migration model. The first (Figure 9) shows a comparison of test analytes in three candidate polymers and their migration rates over 10 days at 20°C.

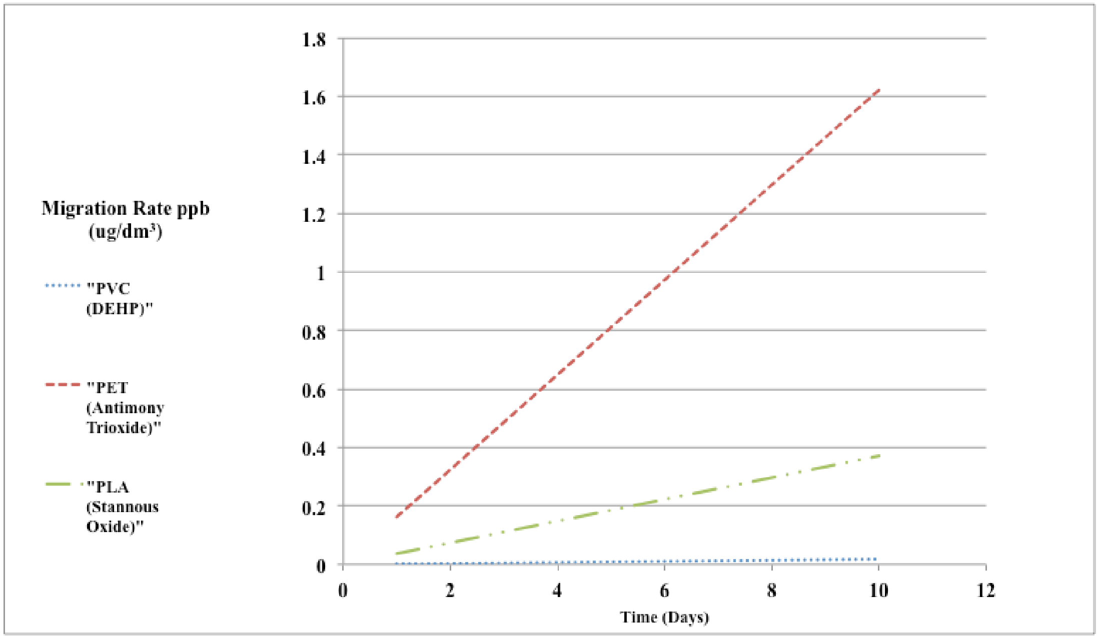


Figure 9. Predicted Migration Rates at 20°C over Ten Days

This graph shows that PET has significantly higher migration rates for its challenge analyte than either PLA or PVC. Table II provides migration rate data for each of the different polymers and analytes for the three challenge temperatures and after 10 days of migration.

A second graph below (Figure 10) shows analyte migration rates for the three polymers at 40°C. As expected migration rates for all three analytes increased with increased temperature.

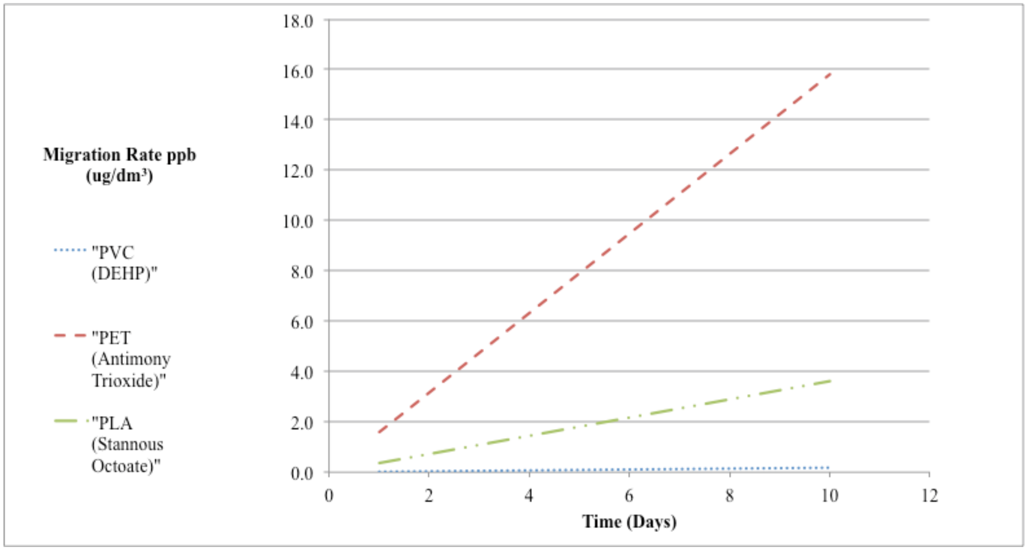


Figure 10. Predicted Migration Rates at 40°C over Ten Days

Again this graph shows that PET has a higher migration rate for antimony trioxide than test analytes in either PLA or PVC as a function of increasing time. This graph also shows that the greatest increase in migration rate occurs in the analyte antimony trioxide, which you can see in Table II. The last graph (Figure 11) shows migration rates for test analytes in the three polymers at 121°C.

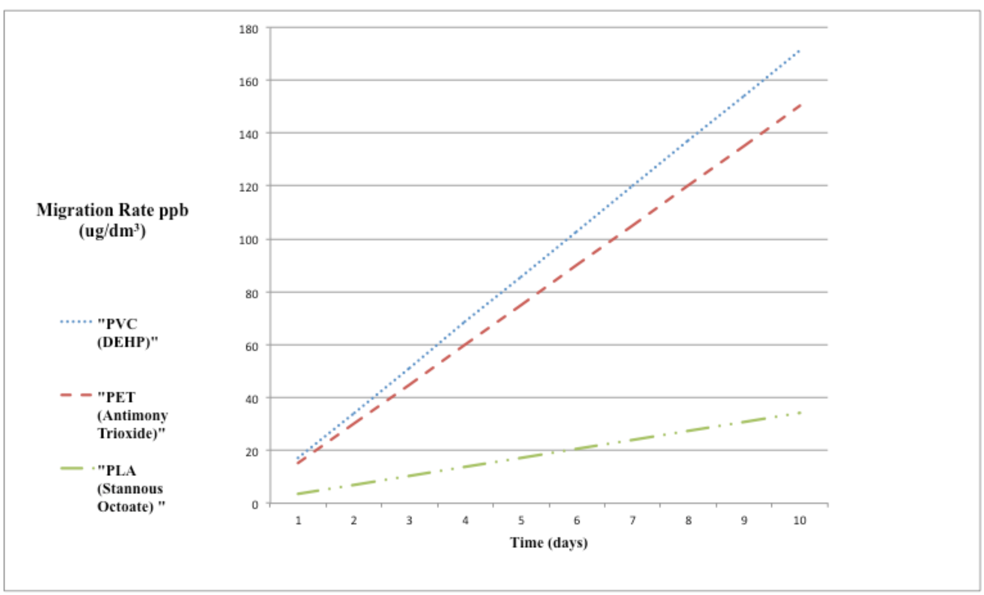


Figure 11. Predicted Migration Rates at 121°C over Ten Days

In comparing all three graphs (Table II) you can see in all cases, as temperature

increases migration rates increase. The greatest change in migration rate occurs between 40°C and 121°C in PVC's challenge analyte, DEHP (171 ug/dm^3). This increase causes PVC to have an accelerated migration rate at 121°C. As temperatures increase PET and PLA become more similar with respect to their migration rates.

Table II. Comparison of Ten Day Migration Rates (ug/dm^3)

Temperature	PVC	PET	PLA
20°C	0.019	1.62	0.37
40°C	0.18	15.81	3.62
121°C	171.4	150.4	34.4

These data also show that as temperatures increase, migration rates continue to increase indicating that a terminal migration rate was not achieved in ten days. In order to test terminal migrations rates actual kinetic experiments must be conducted. Similar models are currently used by FDA to predict and estimate migration rates for a large number of potentially harmful polymer constituents.

Discussion of Polymer Constituent Behaviour

DEHP

Polyvinyl chloride is a polymer that uses an organic plasticizer DEHP (Figure 12[31]). DEHP is a large organic compound.

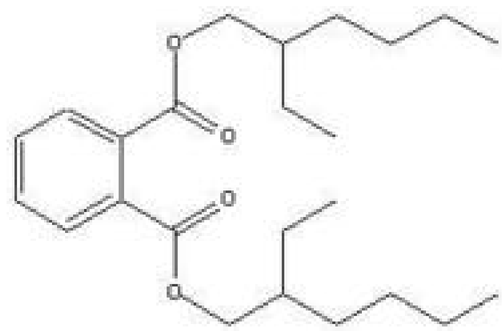


Figure 12. DEHP Molecular Structure

Plasticizers embed themselves into the polymeric matrix to spread the matrix, and expand polyvinyl chloride increasing its flexibility. DEHP does not chemically bond to PVC[31]. Since DEHP is embedded, it is constrained from migration at low temperatures. As temperature increases and PVC reaches its glass transition temperature (82°C) the polymer chains begin to become more flexible, mobilizing DEHP, and allowing it to migrate at higher rates. These models were developed without dependence on any specific polymer substrate. DEHP is lipid soluble. In the presences of oily or fatty substrates, DEHP is likely to migrate even more quickly due to lipophilicity with contained liquids[31].

Antimony trioxide

Antimony trioxide is dispersed in ethylene glycol when used as a polymerization catalyst. It is an inorganic compound with low particle size. Antimony trioxide is often left near the plastic surface after manufacturing, which may be why it exhibits higher migration rates at low temperatures[14]. As

temperature increases, migration rates increase. Since the majority of antimony trioxide is on the surface of the plastic, this increase is not a significant as the increase of DEHP, which is governed by different migration mechanisms. Once the near surface antimony trioxide is depleted, migration should slow.

Since antimony trioxide has the smallest molecular weight as well as a lower glass transition temperature (Table III), molecules move between the PET chains easily. As temperature increases PET has a gradual increase unlike PVC which accelerates drastically at 121°C. It would seem that PET migration increases as temperature rises purely because the molecules move faster at higher temperatures allowing for the small antimony trioxide molecules to migrate at higher rates.

Stannous Octoate

Stannous octoate is an organo-metallic compound used to remove water during polylactic acid, open-ring polymerization[32]. However it is not possible to remove all the excess water in this process, which causes some of the stannous octoate to remain in the polymer. As temperatures increase migration rates increase due to molecular mobility. Polylactic acid also has a lower concentration of stannous octoate than either of the other analytes in their respective polymers, so there is less material to migrate. This may account for stannous octoate having the lowest migration rates at increasing temperatures. PLA is a biodegradable polymer, and under the right conditions can break down in 60 days (ASTM 5336)[33]. PLA is 20-30% crystalline and is therefore more crystalline than PVC, but less crystalline than PET[33]. PLA also has the lowest glass transition temperature of the three polymers (Table III), which could contribute to higher migration rates at lower temperatures. As temperature increases, the migration rate stays relatively low compared to the other polymers, which may be caused by the glass transition temperature. Another possibility is that stannous octoate has the highest molecular weight of the three analytes. This makes it less mobile within the polymer and causes lower migration rates.

Stannous octoate is still being tested for migration, and few kinetic

experiments have been conducted to actually measure migration rates.

Table III. Polymer Properties

	PVC	PET	PLA
Crystallinity (%)	10	45	20-30
Analyte molecular weight	390.57	291.52	405.1
Glass Transition Temperature (C)	82	78	58

Conclusions

- PET has a higher migration rate for antimony trioxide, than polyvinyl chloride (for DEHP) and polylactic acid (for stannous octoate) at the two lower temperatures computed (20°C and 40°C).
- At higher temperatures (121°C), polyvinyl chloride has a much higher migration rate for DEHP than polyethylene terephthalate (for antimony trioxide) and polylactic acid (for stannous octoate).
- With currently available data, biodegradable PLA has the lowest migration rate at the highest temperature calculated, (121°C)
- Isothermal rate predictions are approximate because factors such as sunlight, polymer length (number and weight average molecular weights), fluid substrates, *etc.*, can affect migration rates.

Recommendations

- Conduct designed migration tests with PLA similar to PVC and PET testing.
- Expand models to account for additional factors that can affect analyte migration, such as polymer degradation, biodegradation, phase transitions, and surface escape rates.

Results and Discussion – Cost Model

After observing the process to manufacture 2.5 ounce bottles of ID Millennium lubricant at Westridge Laboratories, we found that the cost model behaved predictably. Materials cost is distributed in manufacturing steps, but labor and overhead costs are uniformly distributed throughout the process. Because of this, the most costly steps are the most labor-intensive procedures. This cost model provides a good general background to compute expected production costs.

Cost estimates were, as expected, predictive of overall final production costs. However, in order to refine cost models, additional elements could be added. Implementing ergonomic recommendations are an additional cost, which is not captured in this study.

The Westridge process is already very efficient. The majority of problems with the product can be controlled by visual observation. The current supervisory method of quality control is effective. Operators are familiar with the product and quality standards required for Westridge products.

One change, which would improve the process, would be to document quality errors that occur frequently. By documenting quality problems, areas for improvement could be discovered. Quality of the lubricant itself is something we did not address in this study.

Productivity in the manufacturing facility is most efficient with four operators working at one time: one operator filling, two operators capping, and one operator uncapping. After one operator has completed a leak test, two operators must recap product bottles, and an additional operator boxes finished cases. Each of these operators is assigned their tasks to provide a constant production rate, a rate that produces approximately 8 cases/hour, excluding set up time.

Based on this cost model, the most expensive manufacturing step is labor cost associated with batch size. For small batches, the most costly step is set up. For larger batches, the major steps that affect cost are capping and recapping bottles. This is due to the fact that capping requires two operators. The two operators are cost effective because at increased production rates, fewer bottleneck shut down the capping station.

Westridge must produce at least two cases per order. By only producing one case, efficiency and profitability are reduced due to higher labor demands and material costs.

Based on our observations, we did not identify any unusual conditions in the manufacturing process that could be altered to improve productivity. The process utilizes automated machines that are assisted by human operators. Working conditions appeared acceptable and are designed to promote productivity.

Some collected data were difficult to interpret. Since we were not able to time each bottle individually, it took additional effort to interpret and cross compute this data. Some parts of the process were also difficult to include, due to the fact that operators were exchanged periodically, which increased and decreased the production rate. However, by averaging the number of employees used at any point in the process, we were able to integrate production steps. It was also somewhat difficult to assess all costs and effort utilized outside the manufacturing area. Some additional costs may need to be considered.

Once the product has been packaged, the remainder of the process was not timed and documented. To further examine the Westridge process, time studies should be conducted to determine the average time to ship an order. If Westridge is using First In First Out (FIFO), or First In Last Out (FILO) materials management, that will affect inventory cost models. The average time to process an order should be timed. This step should be included in the total time to process an order because it can provide the delay between when an order is received and when the manufacturing area begins production. By including these steps in the cost model, the full process would be analyzed from order entry to product shipment from the warehouse.

Based on this cost model, Westridge can improve manufacturing efficiency and minimize product movement within the process. This would reduce intra-plant travel time and increase production per labor unit.

This cost model should only be used as guidance for Westridge to consider in developing its own operating cost models. This is a best-efforts cost estimation based on limited resources for the students involved, and limited access to

planning data, materials cost, and new products under development.

Conclusion

- The most costly part of the Westridge manufacturing process appears to be set up time, and capping/recapping operations.
- This manufacturing process could be improved by utilizing both production lines and implementing new ergonomic controls.
- To increase efficiency, and minimize unnecessary travel time while working on the assembly line, Westridge should implement rapid order entry to the production floor, and optimize individual production steps.
- With slight alterations, this cost model can be used to determine the total cost of similar products produced by Westridge Labs.

Recommendations

- Improving ergonomic controls in the work area could decrease employee fatigue and increase production.
- Westridge should utilize all equipment on the manufacturing floor instead of single manufacturing lines, and increase batch size, to improve profitability.
- Operators should stay in their designated work areas, which minimizes unnecessary movement.

Broader Impacts

Plastics are an ever-growing industry in our world. As we decrease the use of natural resources such as wood, we increase production of plastics. With this increased production come consequences that are not yet fully understood. This project focused on PET and PVC and possible negative effects from their use. Although direct experimentation was beyond the resources of this project, literature documentation has raised concerns about negative environmental and human impacts from the expanded use of these materials.

Roughly 27% of all used plastic material is actually recycled[1]. Although this is an increase from previous years, it still is a very low amount compared to the volume of waste that we produce. PET makes up the majority of recycled plastic, but the amount of PVC recycled is miniscule. Less than 8% of used PVC is recycled[9]. Plastic that does not get recycled, ends up in landfills or is incinerated. Approximately 18% of all used plastic ends up in our oceans[30].

The world produces approximately 23 million tons of PVC a year[31]. In 2000 we were only producing 3 million tons. PVC can be found in building materials, medical supplies, packaging, toys and many other products. A main plasticizer in PVC is bis (2-ethylhexyl) phthalate (DEHP). DEHP studies have shown negative health effects. DEHP is a potential human carcinogen and it is likely to have teratogenic effects on male and female embryos[34]. Some phthalates have been restricted from children's toys in Europe since 1999, and starting in a 2009 regulatory levels of 0.1% mass weight cannot be exceeded in some phthalate plasticizers used in toys that can enter the mouths of children[35]. PVC can also degrade, causing phthalate to leach into soil and air from landfills[11]. In 2009 some phthalates were restricted in children's toys sold in California (DEHP, along with dibutyl phthalate (DBP), benzyl butyl phthalate (BBP), diisononyl phthalate (DINP), diisodecyl phthalate (DIDP), and di-n-octyl phthalate (DnOP))[36].

As health and environmental concerns about PVC increase new plastic are beginning emerge as replacements. The main plastic that has begun to replace PVC is PET.

PET is used in applications such as plastic bottles for drinking, packaging, children's toys and many others[9]. There has been little research on chronic health effects to determine if PET is an acceptable replacement. Current research has shown that PET contains a potential toxin, antimony trioxide. Chronic effects of antimony trioxide have not been adequately studied, but could include stomach pains and vomiting. Antimony trioxide has also shown signs of respiratory problems, decreased longevity, diffused fibrosis and obstruction of lung function[34]. This Senior Project illustrates why new materials (like PLA), and new ways to package commercial items are important to human health and to the natural environment.

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Appendices

Appendix A – Cost Model Sample Spread Sheet

Cost Model			
If Westridge wants to make 'x' amount of 2.8 oz. bottle of ID Moments how long will it take and how much will it cost?			
Input			
Batch size (number of bottles)	240		
Output			
Number of cases required	10		
Overhead cost	$453.38		
Raw material cost	$179.09		
Labor cost	$59.08		
Total Cost	$691.56		
Revenue ($)	$2,380.80		
Profit ($)	$1,689.24		
	Seconds per batch	Minutes per batch	Hours per batch
Time to complete (sec, min, hour)	5054.45	84.24	1.40
Additional Output			
Cost per individual step			
	Seconds per batch	Minutes per batch	Hours per batch
Set up cost ($)	$15.43		
Number of operators	4		
Time to set up (sec, min, hour)	1320	22	0.37
Cost to label ($)	$15.53		
Number of operators	2		
Time to label (sec, min, hour)	510.14	8.50	0.14
Cost to fill ($)	$148.84		
Number of operators	1		
Time to fill (sec, min, hour)	794.78	13.25	0.22
Cost to cap ($)	$21.79		
Number of operators	2		
Time to cap (sec, min, hour)	779.53	12.99	0.22
Cost to wait ($)	$3.86		
number of operators	1		
time to wait	1320	22	0.37
Cost to box ($)	$3.76		
Number of operators	1		
Time to box (sec, min, hour)	330	5.5	0.09
Total cost ($)	$209.21		
Total time (hours)	1.40		

Variable Values				
Factors included in cost model:			Sq. Feet	Rate
overhead (rent per month)		$232,500.00	1500	$155.00
cost of raw materials per case		$17.91		
Average hourly wage (including taxes and benefits)		$10.52		
Average employees working on 2.5 oz ID Millennium		4.00		
Allowance		10%		
	$322.92			
Time per step				
		Seconds per bottle	Seconds per case (24 bottles)	Fixed Time (sec)
Set up time (sec)				1200
Time to label (sec)		1.93	46.38	
Time to fill (sec)		3.01	72.25	
Time to cap (sec)		2.95	70.87	
Time to uncap (sec)		0.00	0.00	
Time to recap (sec)		0.00	0.00	
Time to box a case (sec)		N/A	30	
Wait time on conveyer (sec)		5	120	
Time per step including allowances				
		Seconds per bottle	Seconds per case (24 bottles)	Fixed Time (sec)
Set up time (sec)				1320
Time to label (sec)		2.13	51.01	
Time to fill (sec)		3.31	79.48	
Time to cap (sec)		3.25	77.95	
Time to uncap (sec)		0.00	0.00	
Time to recap (sec)		0.00	0.00	
Time to box a case (sec)		N/A	33	
Wait time on conveyer (sec)		5.5	132	
Cost of a bottle of 2.5 oz Millenium ($)			$9.92	
# in case			24	
Average number of bottles labeled per minute		31.05		
Average number of bottles filled per minute		19.93		
Average number of bottles placed on line per minute		20.32		
Average number of bottles uncapped per minute		20.92		
Average number of boxes filled per minute		2		
Cost of Raw Materials ($)				
Back Label ($)		$0.02		
Front Label ($)		$0.03		
Bottle ($)		$0.10		
Cap ($)		$0.07		
Product ($) Includes waste and overfill		$0.51		
Cap Liner ($)		$0.01		
Case Box ($) one for each 24 bottles		$0.28		

Appendix B – Example of a Direct Time Study Spreadsheet

Minutes	# of employees	Number of Bottles Filled	# of bottles capped	# of employees	# uncapped	Time of Day	Total employees	Notes
1	1	0	8	2	34	07:55 AM	3	
2	1	0	0	2	20	07:56 AM	3	took sealer off, poured back into lubricant container
3	3	9	4	0	0	07:57 AM	3	no more bottles coming down line
4	3	28	20	0	0	07:58 AM	3	
5	3	29	20	1	19	07:59 AM	4	
6	3	26	26	1	28	08:00 AM	4	
7	3	26	25	1	22	08:01 AM	4	
8	3	29	26	1	20	08:02 AM	4	pick up fallen caps
9	3	26	28	1	23	08:03 AM	4	
10	3	28	28	1	35	08:04 AM	4	
11	3	28	20	1.5	29	08:05 AM	4.5	
12	3	6	11	0	0	08:06 AM	3	pick up fallen caps
13	3	0	10	1	29	08:07:00 AM	4	cleaning bottles
14	3	28	28	1	16	08:08 AM	4	got additional trash bag for caps
15	3	26	17	1	17	08:09 AM	4	Switch Positions
16	3	0	0	1	13	08:10 AM	4	
17	3	14	0	1	18	08:11 AM	4	
18	2	26	7	1	0	08:12 AM	3	record information on data sheet
19	3	27	14	0	0	08:13 AM	3	
20	3	26	21	1	14	08:14 AM	4	
Total		382	313		337			
Average	2.75	19.1	15.65	0.925	16.85		3.675	