



Accounting for the benefits of technology change: Replacing a zinc-coating process by a water-based organo-metallic coating process



C.M.V.B. Almeida^a, F. Sevegnani^a, F. Agostinho^a, Gengyuan Liu^{b, c}, Zhifeng Yang^{b, c}, L. Coscieme^a, B.F. Giannetti^{a, b, *}

^a Laboratório de Produção e Meio Ambiente, Programa de Pós-Graduação em Engenharia de Produção, Universidade Paulista, R. Dr. Bacelar 1212, Cep 04026-002, São Paulo, Brazil

^b State Key Joint Laboratory of Environment Simulation and Pollution Control, School of Environment, Beijing Normal University, Beijing, 100875, China

^c Beijing Engineering Research Center for Watershed Environmental Restoration & Integrated Ecological Regulation, Beijing, 100875, China

ARTICLE INFO

Article history:

Received 17 April 2017

Received in revised form

9 August 2017

Accepted 18 October 2017

Available online 27 October 2017

Keywords:

Environmental accounting

Emergy

Metal coating

Cleaner production

ABSTRACT

Technology change is a well-known strategy used by Cleaner Production (CP) practitioners, and it refers to modifications in the process and/or equipment to increase production efficiency and reduce waste and emissions. These changes can range from small, low-cost options to the replacement of processes that involve large capital investments. The improvements and advantages of the new alternatives must be evaluated in a way to measure and assure its real benefits. This work presents an emergy evaluation of a fasteners manufacturing company planning to replace the zinc-coating process by a water-based organo-metallic coating process. Accounting for the use of resources and the environmental services to dilute the Cr (VI) in the effluent, the study shows that the effluent treatment is efficient and that the emergy invested by the environment to dilute the Cr (VI) released is lower than 0.1% of the emergy used in the coating process. The case study is an example of the application and evaluation of CP options (good operational practices, material and raw material changes, technological modifications, and product change) and is presented to motivate product manufacturers to prioritize environmental performance assessments to their products and services equally as well as to save manufacturers substantial time and efforts during their first attempts to implement CP actions.

© 2017 Elsevier Ltd. All rights reserved.

1. Introduction

The application of coatings in steel and other ferrous substrates is established in industry as an effective and reliable way of protection against corrosion. Corrosion problems are frequent and occur in a variety of activities, such as in the chemical, oil, petrochemical, naval, civil construction, automotive, air, rail, subway, maritime, road and media industries, such as telecommunications systems, dentistry, medicine and works of art such as monuments and sculptures (Morcillo et al., 2013).

Much research is coordinated around all over the world to develop new types of coatings that are increasingly resistant and less aggressive to men and environment. Due to its low cost, the zinc coating is widely used though the original electroplating

process used cyanide. Fortunately, these systems are losing ground to alternatives that avoid the use of toxic and harmful substances (Dubent et al., 2010). Processes of acid galvanization offer a glossy finish that competes with that obtained in the nickel-chrome deposit application processes (Balloy et al., 2007). The high-efficiency, acid-based chloride bath saves energy and increases productivity. There are also sulphate-based processes which operate in acidic medium and can be used when the brightness of the coated part is not an important requirement (Ismail et al., 2009).

In the fastener industry, the most used process uses alkaline zinc baths without cyanide, but corrosion resistance is still increased by the application of a conversion layer using hexavalent chromium (García et al., 2013). The chromium-based conversion layer also allows the pieces coloring in blue, yellow, green or black, and the yellow layers the most popular for fasteners because of their brass appearance. The well-documented problems associated with the use of Cr (VI) have encouraged the search for alternatives for its replacement or disposal and are the subject of intensive research in the zinc coating industry (Hadley et al., 2002; Garcia et al., 2013).

* Corresponding author. Laboratório de Produção e Meio Ambiente, Programa de Pós-Graduação em Engenharia de Produção, Universidade Paulista, R. Dr. Bacelar 1212, Cep 04026-002, São Paulo, Brazil.

E-mail address: biafgian@unip.br (B.F. Giannetti).

Nevertheless, many companies still use Cr (VI) conversion layers to achieve the desired coating resistance.

An alternate technology based on organo-metallic coatings was developed in the United States in the mid-1960s is (Nadherny et al., 2012). Although there were still no concerns about the use of chromium in the coatings or its effects on the environment, organo-metallic coatings had great technical and commercial potential, as they combined high performance and low cost for both application and effluent treatment.

Through time, more strict regulations, especially in the automotive industry forcing the auto parts manufacturers to change their production processes in order to achieve compliance (Séby et al., 2008). Technology change is a well-known strategy used by Cleaner Production (CP) practitioners, and it refers to modifications in the process and/or equipment to increase production efficiency and reduce waste and emissions. These changes can range from small, low-cost options to the replacement of processes that involve large capital investments. Thus, the improvements and advantages of the new alternatives must be evaluated in a way to measure and assure its real benefits.

Currently, in the fastener industry (manufacturers of nuts, bolts, rivets), the main alternatives for replacing Cr (VI) can be summarized in two well-defined segments:

- electrodeposited coatings free from hexavalent chromium (Tylus et al., 2015).
- organo-metallic coatings (Duprat and Kelly, 2009).

Some companies experience great difficulties in implementing these practices due to several reasons such as: organizational, technical, and economic barriers (Oliveira Neto et al., 2017) and there are several publications reporting that CP practices are mostly encouraged by coercive and normative pressure (Severo et al., 2015). Companies, are forced either by local government, by their international headquarters or by customers to change their production processes focusing on environmental issues. In the Brazilian automotive sector, the auto manufacturers are the focal companies, which act as central agents that not only encourage, but also impose the pressures faced by other supply chain members. This pressure led to the introduction of the ISO 14001 certifications as well as Environmental Management Systems (EMS), and encouraged several actions to be taken in the automotive supply chain.

The cooperation between academic and industrial sector was reported by Almeida et al. (2013), who have assessed the replacement of lead in solders applied to the electronic industry. Using emergy synthesis and the DALY indicator (Disability Adjusted Life Years) they assessed the impact of different types of solders on the environment and on the human health. The results have shown that lead-free solders require more environmental resources than the tin-lead solders. The same authors (Almeida et al., 2015) have studied the case of a small auto-part company that performed a product change in its production process due to a change in the product of the focal company of the automotive supply chain. Their study shows that technological decisions made by the focal company can affect the other members of the supply chain in different ways.

Oliveira Neto et al., 2016 studied CP practices applied to the truck industry regarding the reduction of the environmental impacts, and reported that very little importance is given to the assessment of the environmental impact that results from CP practices, and that most of the published papers focus on the cost reduction. Among economic and social benefits, the CP practices assessed resulted in almost one thousand tons of raw material not extracted from the nature. In 2017, Oliveira Neto et al. proposed a

framework for the implementation of CP to be applied to small and medium sized enterprises. The framework was validated with the application to four Brazilian companies that belong to metal-mechanical sector. These authors documented the difficulties faced by the small and medium enterprises in Brazil as well as the difficulties for the implementation of CP actions, and introduced the Material Input per Service Unit (MIPS) as a way to measure the environmental issues linked to resource removal from natural ecosystems. The application of the framework to the four enterprises, generated results of annual savings of several base resources, as well as the economic gains due to these savings. Severo et al., 2015 studied the CP actions in the Metal-Mechanic Cluster of Serra Gaúcha, Brazil. Evaluating 298 companies of the cluster and analyzing the relationship between the CP concepts, environmental sustainability and organizational performance, these authors concluded that CP practices influence positively the production capacity and flexibility.

The company in study expressed a strong wish to replace the zinc-coating process by a water-based organo-metallic coating process. A technology assessment was conducted using emergy synthesis to evaluate the efficiency and the disadvantages of the technology change for a fastener industry, member of the Brazilian automotive supply chain. This paper analyzes the use of resources in a non-cyanide alkaline industrial system with chromate conversion coating used by the company and compares with the chrome-free organo-metallic technology. The study includes the emergy relative the ecosystem's services used to dilute the release of toxic substances in the effluent.

2. Method

2.1. Emergy accounting

Emergy accounting is used to evaluate the company in the case study, as it provides strong scientific-based indicators that can assess several aspects of the company's performance. Emergy is the available energy of one kind previously used up directly and indirectly to make a service or product. Its unit is the solar emergy joule, sej. (Odum, 1996). Emergy's logic of memorization rather than conservation is different from other energy-based analyses (Brown and Herendeen, 1996). An emergy synthesis separates renewable (R) from non-renewable inputs (N) and local ($I = N + R$) from external inputs (F). These distinctions allow defining several emergy-based indicators that can support decision making (Brown and McClanahan, 1996) (Fig. 1).

Emergy indicators focus on the aspects of environmental sustainability issues regarding resource use, its origin, and process efficiency in converting inputs into outputs. The total emergy per unit of product or service (UEV expressed in sej/unit) is a measure of global efficiency. The less emergy needed to produce a given amount of product, the more efficient (in relation to the biosphere) the system will be.

The EYR is the ratio of total emergy ($Y = R + N + F$) to the emergy purchased from the market (F). This index shows the efficiency of the system in the use of the available local resources. The EIR quantifies the emergy investment necessary for the operation of the system ($EIR = F/(N + R)$).

Emergy accounting allows the conversion of all contributions received by the production system (metals, energy, oil, money, and even information) on a single basis of measurement: the solar emergy joule (sej). Systems under study can be compared regarding efficiency in resource use, productivity, environmental burden, and global sustainability.

The evaluation procedure applied is performed according to the following steps:

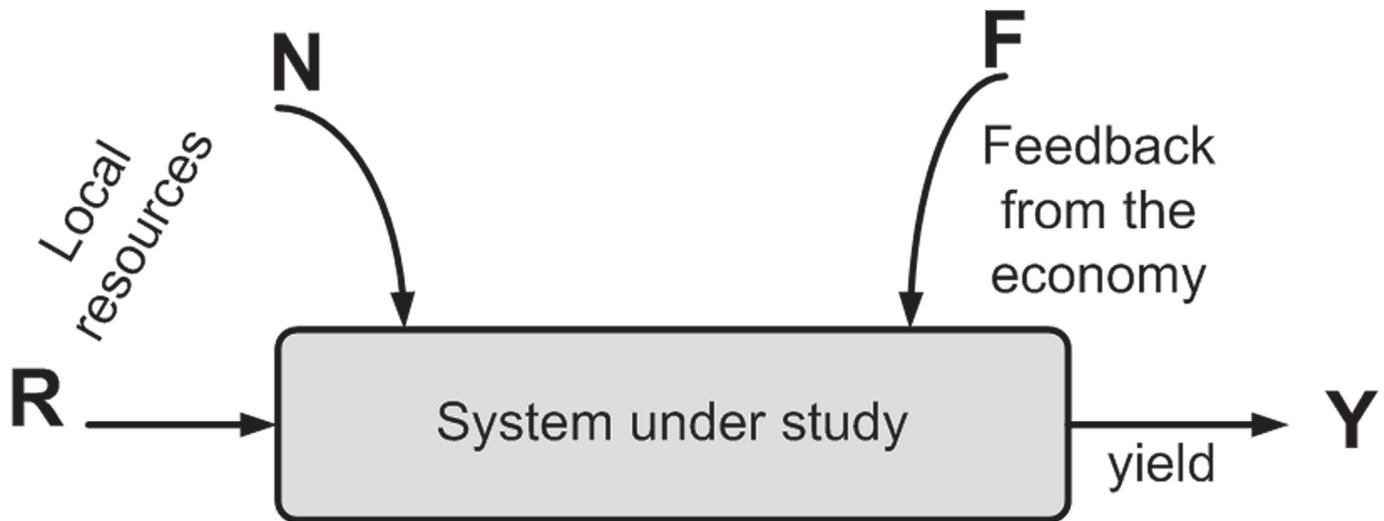


Fig. 1. Three Arm Energy System Diagram. R (renewable resources), N (non-renewable resources), F (feedback from the economy), Y (yield).

- Definition of the system under study to set the boundaries for investigation;
- Study of the context in which the system is inserted and execution of the mass balance;
- Elaboration of energy flow diagrams;
- Elaboration of energy tables with data collected;
- Energy Indicators Calculation;
- Discussion for future management actions and decision-making.

2.2. Response from the environment to toxicity and environmental services for dilution

In this paper, two environment services were calculated: the response of the environment to the toxicity of the effluent released and the energy applied to its dilution in one year of operation.

The amount of Cr (VI) present in the effluents generated by the zinc-coating process was used to calculate the response to the toxicity of the effluent and the energy used for its dilution. The company's self-monitoring report indicated that the Cr (VI) concentration was below 0.01 mg/L (Review Report No. 6321 of 02.21.2006 issued by Centralsuper Commerce Chemicals Ltd.), which is the limit for disposal according to current Brazilian law.

The Effluent Treatment Unit (ETU) discards 4000 L of water per hour, and the zinc-coating process discards treated water for 2 h daily for approximately 22 working days per month. The amount of Cr (VI) was calculated to be 0.02112 kg/year.

In order to calculate the emergy regarding the damage to human health or to the number of years that people will not be able to work due to any disability or death (C_j) related to the pollutant release, it is used Equation (1) (Ukidwe and Bakshi, 2004).

$$C_j = m_j \times \text{DALY} \times \tau_{\text{HR}} \quad (1)$$

where:

m_j = mass of the substance released (kg/year)

DALY = value regarding the loss of years of life or death related to the substance that was released. (lost years. Inhabit/kg)

τ_{HR} = emergy of Brasil/inhabitants, 1.54×10^{16} sej/inhabit. year

The chemical energy used to dilute the substances was considered to be at least equal to the Gibbs free energy associated with

the gradient concentration between the effluent and the receiving environment (Equation (2)).

$$E = N \times R \times T \times \ln\left(\frac{C_1}{C_2}\right) \quad (2)$$

where:

E = energy of the damage

N = number of moles of Cr (VI) discharged

R = universal gas constant (8.314 J/mol K)

Temperature T = 298 K

C_1 = concentration of the effluent discharged

C_2 = the local concentration of the substance of interest

3. Results and discussion

The company in study is a big supplier of the automotive industry in São Paulo, Brazil, and it produces nearly 120 tons of zinc-plated fasteners each month. The company aimed to implement the organo-metallic process in combination with the zinc-coating process to comply with the needs of all customers. The aim of the initial project was to produce 45 tons of zinc-coated fasteners and 60 tons of organo-metallic fasteners monthly.

3.1. Emery accounting for the medium-size metal-finishing company for both production technologies

The energy system diagrams are presented in Figs. 2 and 3. Fig. 2 presents the diagram for the zinc-coating process and Fig. 3 the diagram for the organo-metallic process. Both were designed to

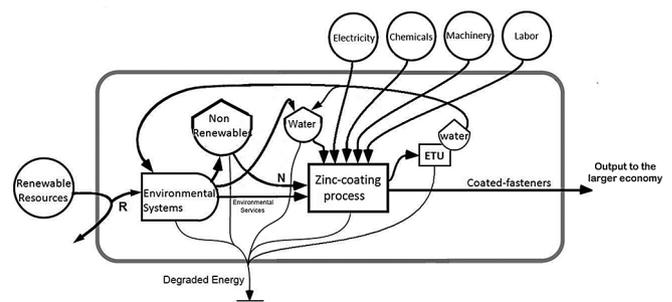


Fig. 2. Energy system diagram of the zinc-coating process.

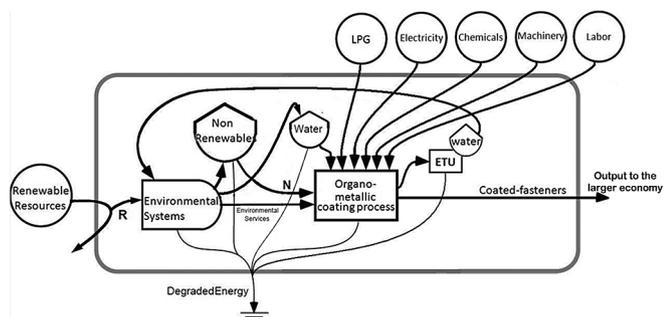


Fig. 3. Energy Diagram of the Organo-Metallic Coating Process. (LPG refers to Liquid Petroleum Gas).

combine information about the systems of interest from various sources and to organize efforts for data gathering. The diagrams show all material and energy flows circulating in both production systems as well as the systems' interactions with the environment. All driving energies from the external economic system (larger economy), the environment, and interactions are included (Odum, 1996). On the left side of the diagram, renewable resources (R) are represented, purchased or imported resources (F) are at the top, and the yield of the system (Y) is represented on the right side, which is the coated fasteners in this case. The diagrams were used to analyze tables of data required for emergy accounting.

The main differences between the two processes are that, the zinc-coating process has an effluent treatment unit (ETU), which feeds part of the water treated back into the production process (Fig. 2) and the organo-metallic coating process (Fig. 3) also has an ETU, but in this case, the water is directly released to the environment after treatment. Both systems have the sludge produced by the ETU as a waste, which is also sold to the ceramic industry. Another difference is that the organo-metallic coating process has an input of LPG, which is used for heating purposes in the cleaning and coating application procedures.

Tables 1 and 2 show all inputs needed for system implementation divided by plant lifetime, annual operating inputs (labor, electricity, machinery, human services), and direct and indirect environmental inputs (water). Suitable UEVs were assigned and resulted in the emergy values in sej after being multiplied by the energy inputs. During the implementation phase, steel was considered a resource from the economy (F) to be incorporated in

the equipment purchased from third parties or in the facility structure. On the other hand, the steel used for the operation was considered a non-renewable resource (N). The water used in the system was taken from an artesian well and was considered a non-renewable resource (N) because the ground water in the city of São Paulo is used faster than its recovery time (Milaré, 1991).

Table 1 shows the flows of materials and energy required for the zinc-coating system. The emergy involved in the coating process as well as the emergy of the coated fasteners were calculated. Column (a) shows the percentage of each item in relation to the total coating process emergy (Y1), while column (b) shows the percentage values corresponding to the total emergy of the coated fasteners (Y2).

In the zinc-coating process, the highest values of emergy are associated with electricity (49%), labor (25%), and chemicals (15%) (column a). Column b of the table shows the steel used to make the fasteners, and the percentages drop to 4% for electricity, 2% for labor, and 1% for chemicals, while 92% of the total emergy corresponds to the steel used to make the fasteners.

The water fed back by the ETU corresponds to 31% of the weight of total water use. Thus, it would be reasonable to suppose that the savings related to its use would also correspond to environmental benefits. In fact, if there were no water reuse, a quantity of 8.4×10^8 g/year could be added to the water input, leading to an emergy contribution of 1.89×10^{14} sej/year to the total emergy of the zinc-plating process; however, as the contribution of water inflow represents only 0.5% sej/sej of the total emergy of the zinc-plating process, this value is not relevant enough to change the UEV of the process, that is, its efficiency.

The influence of the water inflow on the total emergy of the zinc-plated fasteners is even lower at 0.10% sej/sej. Thus, despite an undeniable benefit of saving 840 m³ of a non-renewable resource, this percentage is insufficient to improve the environmental efficiency of the process, and the use of the main inflows (electric energy, chemicals, and man labor) should preferentially be focused on other alternatives.

Table 2 shows the flows of materials and energy that contribute to the organo-metallic coating system. Data were provided by one of the largest Brazilian users of organo-metallic coatings, which has a unit capable of producing about 60 t/month of coated fasteners.

In Table 2, the emergy required by the organo-metallic coating process as well as the total emergy required by the coated fasteners are calculated. In the coating process, the highest values of emergy

Table 1
Material and energy flows for the zinc-coating process.

Description	Unit	Class	Value	UEV (sej/unit)	Emergy (sej/year)	% (sej/sej) ^a	% (sej/sej) ^b	
<i>Implantation</i>								
1	Concrete	g	F	5.94×10^6	1.54×10^9	9.15×10^{15}	5.55%	0.42%
2	Steel	g	F	1.60×10^6	2.77×10^9	4.43×10^{15}	2.68%	0.21%
3	Polypropylene	g	F	1.37×10^5	5.87×10^9	8.04×10^{14}	0.49%	<0.10%
4	Equipment	g	F	5.30×10^4	4.10×10^9	2.17×10^{14}	0.13%	<0.10%
5	Labor	J	F	5.02×10^7	4.30×10^6	2.16×10^{14}	0.13%	<0.10%
6	Machinery	g	F	2.22×10^4	4.10×10^9	9.10×10^{13}	<0.10%	<0.10%
7	PVC	g	F	1.15×10^4	5.87×10^9	6.75×10^{13}	<0.10%	<0.10%
8	Water	g	N	2.70×10^7	2.25×10^5	6.08×10^{12}	<0.10%	<0.10%
9	Rubber	g	F	1.00×10^3	4.30×10^9	4.30×10^{12}	<0.10%	<0.10%
<i>Operation</i>								
10	Electricity	J	F	4.95×10^{11}	1.65×10^5	8.17×10^{16}	49.52%	3.78%
11	Labor	J	F	9.80×10^9	4.30×10^6	4.21×10^{16}	25.52%	1.95%
12	Chemicals	g	F	2.55×10^7	1.00×10^9	2.55×10^{16}	15.45%	1.18%
13	Water	g	N	3.67×10^9	2.25×10^5	8.26×10^{14}	0.50%	<0.10%
	Energy (process)	kg	Y1	7.2×10^3	2.29×10^{13}	1.65×10^{17}	100.00%	–
14	Steel	g	N	7.20×10^8	2.77×10^9	1.99×10^{18}	–	92.13%
	Energy (fasteners)	kg	Y2	7.27×10^5	2.97×10^{12}	2.16×10^{18}	–	100.00%

^a Considering items from 1 to 13.

^b Considering items from 1 to 14.

Table 2
Material and energy flows for the organo-metallic coating process.

Description	Unit	Class	Value	UEV (sej/un)	Emergy (sej/year)	% (sej/sej) ^a	% (sej/sej) ^b
<i>Implantation</i>							
1 Concrete	g	F	3.50×10^6	1.54×10^9	5.39×10^{15}	0.96%	0.21%
2 Equipment	g	F	5.58×10^5	4.10×10^9	2.29×10^{15}	0.41%	<0.10%
3 Steel	g	F	2.00×10^5	2.77×10^9	5.54×10^{14}	0.10%	<0.10%
4 Machinery	g	F	1.10×10^5	4.10×10^9	4.51×10^{14}	<0.10%	<0.10%
5 Labor	J	F	5.02×10^7	4.30×10^6	2.16×10^{14}	<0.10%	<0.10%
6 Rubber	g	F	5.00×10^4	4.30×10^9	2.15×10^{14}	<0.10%	<0.10%
7 Polypropylene	g	F	2.00×10^4	5.87×10^9	1.17×10^{14}	<0.10%	<0.10%
8 Water	g	N	3.50×10^6	2.25×10^5	7.88×10^{11}	<0.10%	<0.10%
<i>Operation</i>							
9 Electricity	J	F	1.50×10^{12}	1.65×10^5	2.48×10^{17}	43.97%	9.69%
10 LPG	J	F	3.89×10^{12}	4.80×10^4	1.87×10^{17}	33.16%	7.30%
11 Labor	J	F	2.29×10^{10}	4.30×10^6	9.85×10^{16}	17.46%	3.85%
12 Chemicals	g	F	2.20×10^7	1.00×10^9	2.20×10^{16}	3.90%	0.86%
13 Water	g	N	2.64×10^8	2.25×10^5	5.94×10^{13}	<0.10%	<0.10%
Emergy (process)	kg	Y1	3.00×10^3	1.88×10^{14}	5.64×10^{17}	100.00%	–
14 Steel	g	N	7.20×10^8	2.77×10^9	1.99×10^{18}	–	77.73%
Emergy (fasteners)	kg	Y2	7.23×10^5	3.54×10^{12}	2.56×10^{18}	–	100.00%

^a Considering items from 1 to 13.

^b Considering items from 1 to 14.

are related to electricity (44%), liquid petroleum gas LPG (33%), labor (17%), and chemicals (4%) (column a). Column (b) includes the number of produced fasteners, and the percentages are 10% for electricity, 7% for LPG, 4% for labor, and 1% for chemicals. The steel used to manufacture the fasteners corresponds to 78% of the total emery.

Table 3 summarizes the results of both processes and shows that less emery is required by the zinc-coating process. That is, fewer resources are used to obtain fasteners using this process. The organo-metallic coating has a total emery of about eight times higher than the zinc-coating process in producing 1 kg of coated-fasteners, and the fasteners obtained through this process use about 19% more resources per year than zinc-coating.

3.2. Unit emery values (UEVs) calculation

For the evaluation of each process, 727,200 kg/year of zinc-coated fasteners (Table 1) and 723,000 kg/year of organo-metallic coated fasteners (Table 2) were considered in the emery accounting. In order to fulfill the aim of the project to produce 45 tons of zinc-coated fasteners and 60 tons of organo-metallic fasteners monthly, the quantity of zinc-coated fasteners equaled 545,400 kg/year, and the quantity of organo-metallic coated fasteners equaled 723,000 kg/year. Table 4 shows the UEVs for each process that were calculated dividing the Emery of the process, retrieved from Tables 1, 2 and A1 (Appendix I), by the mass of fasteners.

Table 4 shows that the zinc-coated fasteners' UEV is lower than that of the organo-metallic coatings, and it is also lower than that relative to the fasteners produced by the company if the processes were used simultaneously. The results obtained show that regarding the use of resources, it is more advantageous (i.e., higher

global efficiency) to maintain the zinc-coating process technology.

3.3. Emery indices

Once the total number of input flows to the coating processes has been identified and the total emery driving the processes has been calculated, a set of indices and ratios can be calculated. These indices have been shown to be particularly useful when studying processes under human control where a sustainable pattern is not guaranteed and choices must be supported by the careful consideration of several different parameters.

Emery indices provide important information about a system's contribution to the economy (EYR) and its efficiency in the use of local resources (EIR). Table 5 shows the calculated indices for the coated fasteners for both processes separately and if the project were to be implemented by the company.

Table 5 shows that the EYR of the zinc-coated fasteners equals 13, meaning that the zinc-coating process returns 13 times the investment to the economy, while the process of organo-metallic coating aggregates approximately 5 times more emery to the local economy. The higher the value of this index, the greater the return obtained per unit of emery invested. In the combined process planned by the company, there would be a return of four times the investment to the economy. The EIR, expresses the relative dependence on resources coming from the economic system/market. It can be observed that the emery investment ratio of the zinc-coating process is the lowest among the three alternatives, indicating a higher usage of natural resources.

3.4. Extending the evaluation beyond the borders of the company: the emery invested by the environment to manage the Cr (VI) contained in the effluent

It is worth noting that the organo-metallic coatings were

Table 3
Total emery used to produce zinc-coated and organo-metallic coated fasteners.

	Zinc-coating	Organo-metallic coating
for the process		
Emery/($\times 10^{17}$ sej/year)	1.65	5.64
UEV ($\times 10^{13}$ sej/kg)	2.29	18.80
for the fasteners		
Emery/($\times 10^{17}$ sej/year)	21.60	25.60
UEV/($\times 10^{13}$ sej/kg)	0.29	0.35

The planetary baseline used was 9.44×10^{24} sej/year.

Table 4
Emery and UEVs for the zinc-coated fasteners, the organo-metallic coated fasteners, and the combination of both processes (Project).

	Zinc-coated (Table 1)	Organo-metallic coated (Table 2)	Project (Table A1)
Emery/(sej/year)	2.16×10^{18}	2.56×10^{18}	4.64×10^{18}
UEV/(sej/kg)	2.97×10^{12}	3.54×10^{12}	3.65×10^{12}

Table 5

Energy indices for the coated fasteners produced by the zinc-coating process, organo-metallic coating process, and produced by the company, which includes with both processes (Project).

Energy indices	Zinc-coated (Table 1)	Organo-metallic coated (Table 2)	Project (Table A1)
Energy yield ratio (EYR ^a)	13.14	4.54	4.05
Energy Investment ratio (EIR ^a)	0.08	0.28	0.33

^a EYR = Y/F; EIR = F/(R + N).

suggested by the automotive industry as an environmentally friendlier solution to replace the zinc-coating processes. The major advantage is associated with the absence of chromium in the effluents of the production process. The calculation of the UEVs indicates that the zinc coating process is more efficient in terms of resource use.

Environment services that naturally treat effluents include the removal and immobilization (even bioaccumulation) of substances and the response of the environment to toxicity. Once emitted to the environment, all substances may be diluted by ecosystem services, such as wind and water flows, to a local concentration. Several factors, such as spatial and temporal dispersion, diffusion, and atmospheric chemistry, are crucial in the determination of the local concentration. If the concentration of the substance emitted is greater than the local concentration value, the emission will cause harm to humans and to the ecosystem. The damage itself is therefore dependent on the existence of pollutants in the ecosystem and on human exposure to the pollutants.

Equation (1) resulted $1,12 \times 10^{14}$ sej/year. This value represents the emergy cost due to the emission of the chromium in its hexavalent form in the generated waste (Genoni et al., 2003). This emergy cost represents the response of the environment to the toxicity of the discharged effluent.

Equation (2) was used to calculate the energy to dilute the chromium emission in its hexavalent form in the effluent. The local concentration used (0.005 mg/L) refers to the concentration of Cr (VI) in urban areas because the company is located in Diadema, Brazil (Silva and Pedrozo, 2001). Thus, for 2.11×10^{-2} kg/year (0.41 mol/year), the chemical energy for the dilution of 0.01 mg/L is 704 J/year. To calculate the emergy invested by the environment in the dilution of Cr (VI) in the effluent, the energy value was multiplied by the UEV for the dilution (1.99×10^{10} sej/J) of the hexavalent chromium that was calculated by Genoni et al. (2003).

Table 6 shows the total emergy invested by the environment to manage the Cr (VI) discarded by the zinc-coating process.

Table 6 includes the emergy invested by the environment to respond to the toxicity of the Cr (VI) released and to dilute it in water bodies. The results show that the total emergy investment is basically unchanged. This indicates that the concentration of Cr (VI) present in the effluent must be close to that of the local concentration and that the treatment of the liquid effluent, which complies with the law, is efficient for minimizing the work and the response of the biosphere. The calculation of emergy invested by the environment to manage the maximum amount discarded in wastewater showed that the value used by the

environment to dilute the toxicity was lower than 0.1% of the emergy demanded in the coating process. It is known that in water bodies in rural areas, for example, the Cr (VI) concentration is no more than 5.00×10^{-6} mg/L (Silva and Pedrozo, 2001); however, using this value as the local concentration base will increase the emergy for dilution to 1.54×10^{14} sej/year, and it still represents no more than 0.1% of the total emergy of the zinc-coating process.

4. Conclusion

The decision to implement either low-cost or high-cost interventions depends on the specific goals of the individual establishment; however, there are rewards that worth when the intervention has a low cost. While good management practices would focus on bringing the production process performance to the designed level, small investments in CP actions may considerably improve environmental performance. This paper presented the experiences of a medium-size company conducting an evaluation to determine whether a change in process technology would be beneficial.

Considering the use of resources to obtain the same amount of product, the methodology indicated that it is best to maintain the zinc-coating process. The calculation of the UEVs showed that regarding the use of resources, the zinc-coating process technology is more efficient in converting global resources into products. Fasteners coated by the zinc-coating process contribute more to the economy (EYR = 13) than the organo-metallic coating process (EYR = 4.5). For the combination process proposed by the company, there would be an increase of almost two times the emergy, from 2.56×10^{18} sej/year to 4.64×10^{18} sej/year. The emergy investment (EIR) is about 3.5 times higher for the organo-metallic coating process when compared to the zinc-coating process, which indicates a better use of resources supplied by the economy by the zinc-coating process.

The calculation of environmental services to assess the toxicity of Cr (VI) in the effluent and its dilution in water bodies showed that the effluent treatment is efficient and that the emergy invested by the environment to manage the amount discarded is lower than 0.1% of the emergy used in the coating process. It should be noted that this evaluation does not consider some important aspects. First, the calculations proposed by Genoni et al. (2003) do not consider the accumulation of Cr (VI) in the water bodies, which should increase the value of the emergy for dilution and the damage to human health, as it reduces the processing capacity of living organisms as a function of time. Similarly, this calculation does not consider the limits of receiving these annual amounts of chromium for the environment.

This work shows that a quantitative assessment is imperative to corroborate decision making. Despite the advantages that were offered by suppliers regarding the elimination of Cr (VI), it was clear that the change in technology would lead to a decrease in global efficiency or to an increase in the use of resources. This increase in resources usage would be higher than the environmental services saved with the avoidance of the toxic release.

Table 6

Emergy related to Cr (VI) discharge by the zinc-coating process.

Description	Class	Emergy/(sej/year)	% (sej/sej)
Zinc-coating process	Y1	1.65×10^{17}	99.92%
Emergy to respond to toxicity	R	1.12×10^{14}	0.07%
Emergy for dilution	R	1.40×10^{13}	0.01%
Total	Y1	1.65×10^{17}	

Appendix I

Table A1
Material and energy flows for the project process.

Description	Unit	Class	Value	UEV (sej/un)	Emergy (sej/year)	% (sej/sej) (a)	% (sej/sej) (b)	
<i>Implantation</i>								
1	Concrete	g	F	9.43×10^6	1.54×10^9	1.45×10^{16}	1.26%	0.31%
2	Steel	g	F	1.80×10^6	2.77×10^9	4.99×10^{15}	0.43%	0.11%
3	Machinery	g	F	6.11×10^5	4.10×10^9	2.51×10^{15}	0.22%	<0.10%
4	Polypropylene	g	F	1.57×10^5	5.87×10^9	9.22×10^{14}	<0.10%	<0.10%
5	Equipment	g	F	1.32×10^5	4.10×10^9	5.41×10^{14}	<0.10%	<0.10%
6	Labor	J	F	1.00×10^8	4.30×10^6	4.30×10^{14}	<0.10%	<0.10%
7	Rubber	g	F	5.10×10^4	4.30×10^9	2.19×10^{14}	<0.10%	<0.10%
8	PVC	g	F	1.15×10^4	5.87×10^9	6.75×10^{13}	<0.10%	<0.10%
9	Water from well	g	N	3.05×10^7	2.25×10^5	6.86×10^{12}	<0.10%	<0.10%
<i>Operation</i>								
10	Electricity	J	F	5.76×10^{12}	1.65×10^5	9.50×10^{17}	82.61%	20.47%
11	Labor	J	F	3.02×10^{10}	4.30×10^6	1.30×10^{17}	11.30%	2.80%
12	Chemicals	g	F	4.11×10^7	1.00×10^9	4.11×10^{16}	3.57%	0.89%
13	Water from well	g	N	3.02×10^9	2.25×10^5	6.80×10^{14}	<0.10%	<0.10%
	Emergy (process)		Y1			1.15×10^{18}	100.00%	–
14	Steel	g	N	1.26×10^9	2.77×10^9	3.49×10^{18}	–	75.22%
	Emergy (fasteners)		Y2			4.64×10^{18}	–	100.00%

References

- Almeida, C.M.V.B., Madureira, M.A., Bonilla, S.H., Giannetti, B.F., 2013. Assessing the replacement of lead in solders: effects on resource use and human health. *J. Clean. Prod.* 47, 457–464.
- Almeida, C.M.V.B., Carvalho, N., Agostinho, F., Giannetti, B.F., 2015. Using emergy to assess the business plan of a small Auto-parts manufacturer in Brazil. *J. Environ. Account. Manag.* 3 (4), 371–384.
- Balloy, D., Dauphin, J.Y., Tissier, J.C., 2007. Study of the comportment of fatty acids and mineral oils on the surface of steel pieces during galvanization. *Surf. Coatings Technol.* 202 (3), 479–485.
- Brown, M.T., Herendeen, R.A., 1996. Embodied energy analysis and EMERGY analysis: a comparative view. *Ecol. Econ.* 19, 219–235.
- Brown, M.T., McClanahan, T.R., 1996. EMERGY analysis perspectives of Thailand and Mekong River dam proposals. *Ecol. Model.* 91, 105–130.
- Dubent, S., Mertens, M.L.A.D., Saurat, M., 2010. Electrodeposition, characterization and corrosion behavior of tin–20 wt.% zinc coatings electroplated from a non-cyanide alkaline bath. *Mater. Chem. Phys.* 120 (2), 371–380.
- Duprat, J.-J., Kelly, M., 2009. Dedicated processes for electroplating on fasteners. In: National Association for Surface Finishing Annual Technical Conference 2009, SUR/FIN 2009, pp. 481–493.
- García, V., Steeghs, W., Bouten, M., Ortiz, I., Urtiaga, A., 2013. Implementation of an eco-innovative separation process for a cleaner chromium passivation in the galvanic industry. *J. Clean. Prod.* 59, 274–283.
- Genoni, G.P., Meyer, E.I., Ulrich, A., 2003. Energy flow and elemental concentrations in the steina river ecosystem (black forest, Germany). *Aquat. Sci.* 65, 143–157.
- Hadley, J., Verberne, W., Wing, L., O'Grady, J., 2002. Corrosion resistance without hexavalent chromium–new zinc plating systems. *Metal. Finish.* 100, 33–36.
- Ismail, I., Nabil, A.-M., Fateen, S.-E., Abdelazeem, W., 2009. Treatment of a synthetic solution of galvanization effluent via the conversion of sodium cyanide into an insoluble safe complex. *J. Hazard. Mater.* 166 (2), 978–983.
- Milare, E., 1991. Brazilian Environmental Legislation. Edições APMP, São Paulo.
- Morcillo, M., Chico, B., Díaz, I., Cano, H., de la Fuente, D., 2013. Atmospheric corrosion data of weathering steels. *A Rev. Corros. Sci.* 77, 6–24.
- Nadherny, L., Sofer, Z., Sedmidubsky, D., Jankovsky, O., Mikulics, M., 2012. ZnO thin films prepared by spray-pyrolysis technique from organo-metallic precursor. *Ceramics-Silikaty* 56 (2), 117–121.
- Odum, H.T., 1996. *Environmental Accounting: Emergy and Environmental Decision Making*. Wiley, New York.
- Oliveira Neto, G.C., Vendrametto, O., Naas, I.A., Palmeri, N.L., Lucatto, W.C., 2016. Environmental impact reduction as a result of cleaner production implementation: a case study in the truck industry. *J. Clean. Prod.* 129, 681–692.
- Oliveira Neto, G.C., Leite, R.R., Shibao, F.Y., Lucato, W.C., 2017. Framework to overcome barriers in the implementation of cleaner production in small and medium-sized enterprises: multiple case studies in Brazil. *J. Clean. Prod.* 142, 50–62.
- Review Report No 6321 of 02.21, 2006. Issued by Centralsuper Commerce Chemicals Ltd. Available at: http://www.unip.br/ensino/pos_graduacao/strictosensu/eng_producao/download/eng_josefernandofaro.swf.
- Séby, F., Castetbon, A., Ortega, R., Guimon, C., Niveau, F., Barrois-Oudin, N., Garraud, H., Donard, O.F.X., 2008. Development of analytical procedures for the determination of hexavalent chromium in corrosion prevention coatings used in the automotive industry. *Anal. Bioanal. Chem.* 391 (2), 587–597.
- Severo, E.A., Guimaraes, J.C.F., Dorion, E.C.H., Nodari, C.H., 2015. Cleaner production, environmental sustainability and organizational performance: an empirical study in the Brazilian metal-mechanic industry. *J. Clean. Prod.* 96, 118–125.
- Silva, C.S., Pedrozo, M.F., 2001. Ecotoxicologia do cromo e seus compostos. Série Cadernos de Referência Ambiental. In: Centro de Recursos Ambientais – CRA, vol. 5. Salvador, Brazil.
- Tylus, W., Winiarski, J., Szczygieł, B., 2015. Evaluation of the growth mechanism of conversion coatings using XPS. *Solid State Phenom.* 227, 159–162.
- Ukidwe, N.U., Bakshi, B.R., 2004. Thermodynamic accounting of ecosystem contribution to economic sectors with application to 1992 U.S. Economy. *Environ. Sci. Technol.* 38, 4810–4827.