Environmental Effects of Alkaline Degreasing for Automotive, Boat and Machine Industry Purposes

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Abstract: We focus on the alkaline degreasing process, for the cleaning of the aluminum, iron and steel products, used in automotive, boat manufacturing and machinery applications. The environmental impacts have been evaluated by Life-Cycle Assessment, with a special focus, on the improvement of microbiological contamination as a mitigation option.

Keywords: alkaline degreasing; cleanliness; life-cycle assessment

1 Cleaning

1.1 Introduction

Nowadays, it is common that the parts needed for a given product can be produced from a large number of disparate manufacturing sites, and so, the parts come from different distances, for a given work phase. In the case of cast parts, sand particles from foundry sand, may remain on the surface, after prolonged storage, or rust may appear on the surface due to acidic vapors, steam or salt water. Wood chips and

sawdust from pallet loads may be deposited on parts. Very clean parts are needed for the manufacture of electric drives, batteries and coatings.

During the casting, processing, machining, forming and corrosion protection of various metals during transportation, oil and grease containing substances [1] [2] are often used, the removal of which, is extremely important, before the long-term corrosion protection is developed, coating and surface treatment is carried out, so that the coating formed can adhere to the metal surface and ensure its' lifetime.

The techniques for removing the various types of contamination should be selected on the basis of the properties of the metal and contaminants to be cleaned.

A modern and effective method of removal is washing with aqueous cleaning agents, which can be acidic, neutral or alkaline solutions with various additives to aid washing and prevent damage to the metal [3-5]. The alkaline agents, included in the degreasing agent are sodium hydroxide, sodium carbonate, sodium silicate [6], ethanolamines, and the corrosion inhibitors sodium phosphates, surfactants and detergent surfactants.

If the contamination is a solid, greasy substance at room temperature, a higher temperature cleaning solution is justified, e.g., 40-65°C, depending on the chemical composition of the detergent, its foaming, foam thermal stability (the solution should not foam) [7] [8].

In the case of alkaline degreasing, the effluent generated, when cleaning aluminum [9], iron and steel components is considered as alkaline degreasing waste (EWC 110114), according to the European Waste Catalogue, while acidic degreasing waste, is considered a hazardous waste.

Before coating, surface treatment and painting, a clean surface must be achieved, gradually improving the quality of the surface to which the layer formed can adhere properly, without any barrier to the coating-metal bond. During the spray degreasing process, the solution is applied from nozzles, to the surface of the part to be cleaned, which physically breaks down the layer of dirt covering the part. In dipping degreasing, the degreased layer is placed in a continuous flow of a cleaning solution, where it remains for a given period of time. This solution may contain a much higher proportion of foaming additives. The parts are then rinsed in several steps, to remove the soap adhering to their surface.

1.2 Active Ingredient

The degreasing process reduces the amount of active component during cleaning and therefore needs to be checked and replenished at regular intervals to ensure that the detergent is always in the right concentration and cleaning is effective. The soap formed during the operation must be separated off and larger contaminants, such as wood chips, must be collected on a filter to ensure that it can be used for as long as possible, without damaging pumps or sticking to components. The degreasing

solutions must be changed regularly, as can be seen from the fact that even with the addition of further active substances, cleaning can no longer be effective, and contaminants remain on the surface. The rinse water should also be changed.

The warm environment is conducive to the growth of micro-organisms: mainly bacteria, yeasts and molds. Adding yeasticide, fungicidal and bactericidal additives to degreasers could be an effective control, but these can further degrade the surface quality, inhibit the adhesion of the coating and become embedded in the coating and remain detectable over time. Hydrogen peroxide, a cheap, effective and environmentally friendly disinfectant [10], breaks down into water and oxygen, so no extra material is added to the surface.

If the degreasing agent is sodium carbonate or sodium hydroxide, the solution can be disinfected with sodium percarbonate in one step and the alkalinity of the degreaser can be increased.

1.3 In-Process Control

1.3.1 Active Component

The description of the active substance content of the degreasing solutions is done by scoring by titration of 10 ml of degreasing solution with 0.1 N hydrochloric acid (0.1 mol/l) or sulphuric acid (0.05 mol/l), the score being the number of ml consumed for the given indicator. For the determination of free alkali, titrate the solution with the indicator phenolphthalein from cyclamen to colorless, and for the determination of total alkali, titrate with the indicator bromocresol green from blue through green to yellow, recording the volume of measuring solution consumed.

1.3.2 Microbiological Cleanliness

The two main methods are rapid test and cultivation.

The rapid assay works on the basis that all living cells, including bacteria, have ATP. If the number of bacteria in a given place increases, the amount of ATP increases. The method uses a bioluminescence reaction to detect the number of microbes and ATP. In the presence of ATP and oxygen, D-luciferin forms a rapidly decomposing oxyluciferin complex in the presence of magnesium ions and luciferase, which emits light (560 nm, please see Equation 1), this light intensity is measured by a luminometer and is correlated to the ATP concentration. The unit of measurement is RLU (Relative Lights Unit) from which the relationship between ATP concentration and light emitted can be determined by calibration [11-14].

$$ATP + Luciferin + O_2 \xrightarrow{Luciferase, Mg^{2+}} Oxyluciferin + AMP\ complex + light \quad (1)$$

2 Environmental Impacts

2.1 Materials and Energy

Life-cycle Assessment is a standardized environmental management method according to ISO 14040 and ISO 14044, which quantifies the environmental impacts of a product or service from the initial phase of raw material extraction through the use phase to waste and recycling.

Life-cycle analysis involves collecting life-cycle inventory data and associating the relevant impact factors and impact categories, such as carbon emissions for energy use and global warming as an impact.

The water, energy, chemicals (e.g., sodium hydroxide) used can be classified in the appropriate impact category according to the evaluation method used. For chemical processes, the CML (Table 1) [17] and ReCiPe [18] [19] impact assessment methods are well suited.

But what about microbial contamination, how can it be assessed? There is no impact category for microbial contamination, as life-cycle assessment works with material flows.

2.2 Microbiological Contamination

If there is a specific characteristic of the contaminant (e.g., it produces a carcinogenic toxin), it can be classified in an impact category with toxicity potential. To give another example, biogas production also involves a large number of microbes that break down organic matter and produce electricity from methane, which is considered as renewable energy, and this process can be classified as such if the material flows are known.

In a case where there is no toxin production, no significant gas formation, no mass flow and the solution is in liquid phase, we can define the bacterial contamination as the chemical oxygen demand [20] including all contaminants in the solution.

However, taking into account that the degreasing effluent may contain up to 10% of emulsified fats and oils, the bacterial contamination level is dwarfed and becomes unvaluable.

The real challenge is to investigate how often degreasing baths need to be changed due to bacterial contamination, or how much extra active ingredient or additive needs to be added to the bath, or how much heating as energy is added when preparing a new bath.

Table 1
CML 2016 impact categories (some example)

Impact category		Description	Equivalent
GWP	global warming potential	The contribution of different greenhouse gases to global warming relative to a unit of carbon dioxide	kg CO_2
AP	acidification potential	Acidification relative to sulphur dioxide	kg SO_2
EP	eutrophication potential	The rate of eutrophication	kg phosphate
HTP	human toxicity potential	The maximum permissible concentration of substances toxic to humans in 1,4-dichlorobenzene (DCB) equivalents	kg DCB
TETP	terrestrial ecotoxicity	Toxic substances for flora and fauna, in DCB equivalents	kg DCB
MAETP	marine ecotoxicity		
FAETP	freshwater ecotoxicity		
ADP elements	abiotic depletion sources	Includes a large number of metal ores	kg antimony
ADP fossil	abiotic depleting fossil sources	The contribution of different greenhouse gases to global warming relative to a unit of carbon dioxide	kg MJ

3 Determination of Microbiological Cleanliness

3.1 Method

In the cultivation technique, the sample solutions are diluted with sterile solution under sterile conditions (laminar box, UV lamp), preparing a dilution series of 10 up to 6 dilutions.

1 ml of the solutions is added to a petri dish and covered with colony counting agar. Incubate at 37°C for 2 days and count the number of colonies formed after the incubation period. Count the dilution on which colonies are clearly visible first. The unit of measurement is CFU (Colony Forming Units), the number of colonies counted multiplied by the dilution. The undiluted solution is multiplied by 100, the first solution diluted by 10 is 10^1 or 10, the 6th solution is 10^6 or one million.

For the rapid assay method, HY-Lite Plus Pen test kit (Sigma-Aldrich, Hungary) was used, calibration was performed with HY Lite ATP standard (1 ng/mL) and HY-Lite 2 luminometer was used to determine the contamination of the samples.

Plate Count Agar or PCA (Biolab, Hungary) [21] was melted ready for use for cultivation, sample solutions and sterile buffered peptone water (Biolab, Hungary) diluted samples were processed into the agar in 90 mm PS petri dishes using a pour plate technique and incubated at 37°C for 48 hours. For breeding, buffered peptone water used for dilution was used as a negative control, and fingerprints were used as a positive control by touching the fingers (after 2 hours after handwashing) directly to the agar surface (Figure 1).

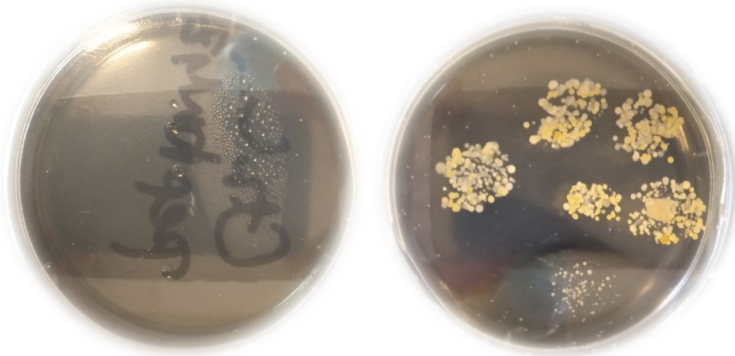

Figure 1
Left: negative control (sterile buffered peptone water) and
Right: positive control with fingerprint

3.2 Results

For transparency, both CFU and RLU units are plotted on the same scale, with off-scale values labelled 90° to the left.

Figure 2 and 3 shows the results of one week a sample (and the weekly rinse water that comes into contact with it). In that the contamination is 26000 RLU with the rapid test method, the highest with this method, while the second rinse phase with the pure plate method shows the highest contamination, 1000000 CFU, i.e., one million colony forming units.

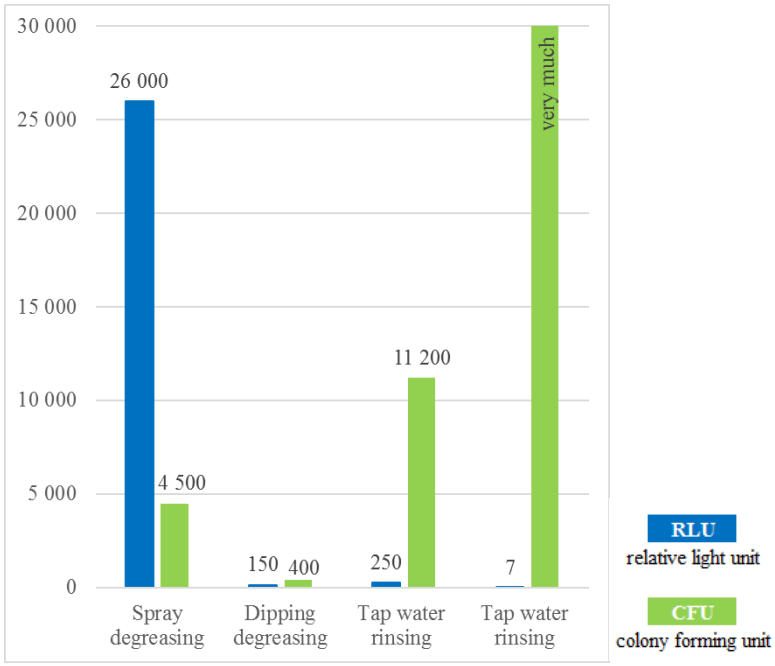

Figure 2
Microbiological contamination after 1 week

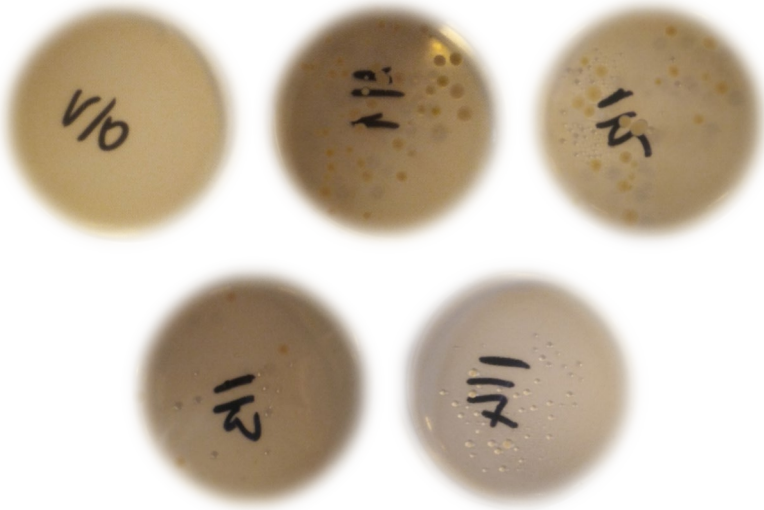

Figure 3
Colonies from 1-week old spray degreasing bath on Plate Count Agar

In Figures 4 and 5 for the 6-week samples, and the contacting weekly effluents, the highest value was 4400 RLU with the rapid test method, which is less than 20% of the one-week, and the highest value with the culture method was undetectable in the first rinse, i.e., more than ten million CFU (>10000000) in the spray degreaser and in the last rinse, which is also in the order of millions.

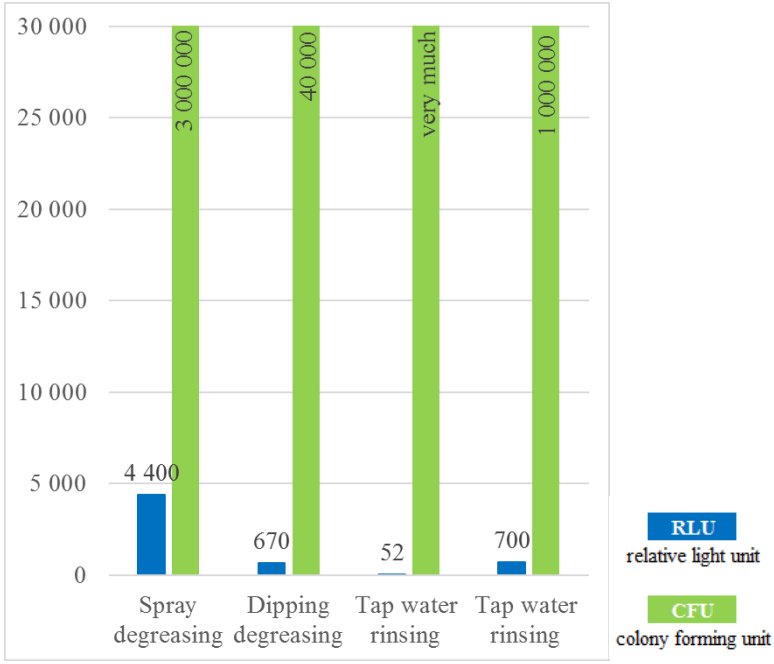

Figure 4
Microbiological contamination after 6 weeks

Figure 5
Colonies from 6-week-old first (tap water) rinsing after dipping degreasing on Plate Count Agar

4 Life-cycle Assessment

4.1 Method

A life-cycle analysis was carried out in software from collected life-cycle inventory data, calculated for 1000 m^2 (thousand square meters). For evaluation, ReCiPe 16 midpoint method was used.

4.2 Results

4.2.1 Energy Consumption, Fossil Fuel Depletion

The distribution of energy consumption is shown in Figure 6. In the plant under study, more than 70% of the energy consumed comes from natural gas, used to heat the degreasing baths. Table 2 shows that the spray and dip degreaser have almost the same energy consumption, more than 2/3 of the energy consumption together.

Table 2
Temperature data

Temperature, °C	Spray degreasing	Dip degreasing	Rinsing, I	Rinsing, II
First sampling, 1 week-old degreasers	52	47	31	20
Second sampling, 6-week-old degreasers	53	45	33	19
6 weeks average	52	45	30	19

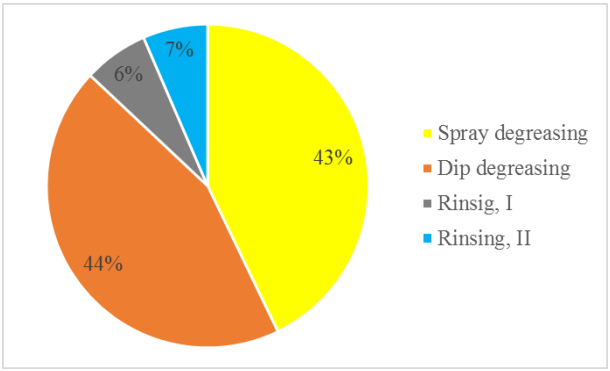

Figure 6
Energy consumption ratio

Reduction could be achieved by using degreasers of the same efficiency, which can operate at lower temperatures, or by using a stronger radius nozzle which can break down the more solid contamination films more easily.

This could be reduced by using solar panels or even by setting up a biogas operation at the site.

4.2.2 Water Consumption

Degreasing chemicals are a significant cost compared to water, which is why you should strive to use a degreasing bath as long as possible, as you can lose active ingredient in one drain, but you also lose the thermal energy stored in the hot water, heating it up takes a long time, and you can't produce in the lost time. The drained degreasing effluent must be transported and treated. It is also important to get the best possible microbiological results to maintain the cleaning efficiency for as long as possible.

The rinse water should be changed weekly, this is important because the surface must be completely clean after degreasing, no soap residues should remain on the surface, as this prevents a good quality coating from forming on the surface.

Figure 7 represents the water consumption ratio. Almost 80% of water is used for rinsing.

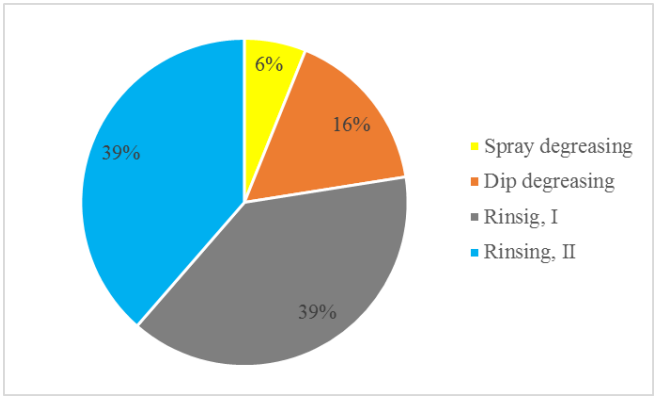

Figure 7

Freshwater consumption ratio

To reduce the amount of rinse water is to control the quality of the parts supplied and improve packaging, as more water is needed to wash down the more contaminated parts. The washing effect is aided by the presence of ions, using rainwater would require adding salts to the rainwater, water storage could also be possible.

4.2.3 Toxicity

Degreasing chemicals contain a variety of substances that are harmful to the environment. There is significant onshore ecotoxicity potential due to surfactants and organic chemicals, with a total of almost 350 kg of 1,4-dichlorobenzene

equivalent due to the two degreasing baths. The freshwater and marine ecotoxicity values are orders of magnitude lower.

Toxicity potentials can be improved by the use of biodegradable substances [23], but it is important to note that their use can impair microbiological purity, as they can be used as nutrients by bacteria, fungi and yeasts.

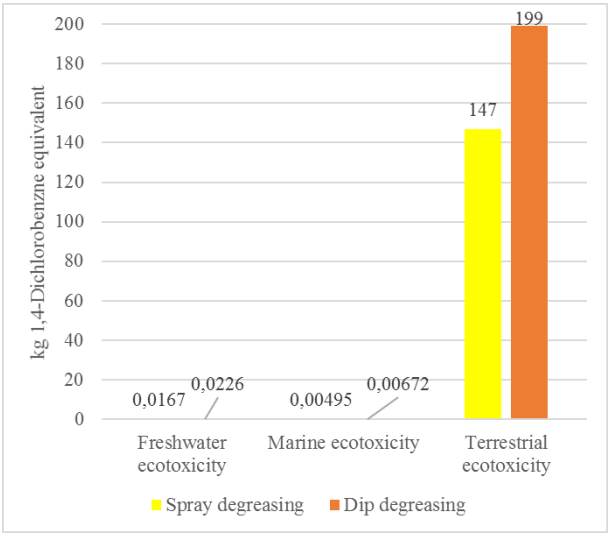

Figure 8
Toxicity values

Conclusions

The presence of microbes in the degreasing samples was detected by culture assay and luminometric ATP-gyroassay. It was found that there is no close correlation, between the two methods. Several strains appeared on agar at the fingerprint site used as a positive control. This also means that extra care should be taken to ensure that workers wear protective gloves. The life-cycle analysis covers energy and material flows, with the degreasing effluents containing organic matter in quantities where the presence of microbes is negligible. However, their presence needs to be addressed due to bath changes, as they can reduce the active ingredient content of the baths, damaging the material to be cleaned. Additional studies are needed to determine which strains are present, so that the amount of bath tanning agents and added chemicals can be reduced.

In terms of energy consumption, heating the degreasing saws consumes more than 2/3 of the energy used, and energy efficiency could be improved by using a domestic biogas plant or solar panels. The rinse water is changed every week and accounts for almost 80% of water consumption. To use rainwater, a tank should be built and the water should be salted, because without salt the rinsing effect is weaker. However, the question of whether the rinse water could be recycled

elsewhere, for example reused to make spray degreasing or dip degreasing baths, should be considered.

Terrestrial ecotoxicity is significant, due to the chemicals used, and could be replaced, by biodegradable or less hazardous substances. The use of biodegradable materials requires caution, as bacteria and fungi can feed on yeasts.

Further studies are needed to optimize the process.

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